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ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS
OF APPLIED CHEMISTRY

Washington and New York
September 4 to 13, 1912

SECTION II: INORGANIC CHEMISTRY

VOL. II

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THE TENSILE STRENGTHS OF THE COPPER-ZINC ALLOYS

By Wilder D. Bancroft and J. M. Lohr
Cornell University.

This investigation is the first to be undertaken to establish the relationship between the constitution of the copper-zinc alloys, and the tensile strength of the cast metal, unworked and without heat-treatment, Mallet,[1] Thurston,[2] Charpy,[3] and the Alloys Research Committee[4] have all done work on the tensile strength of the brasses, but their work has differed in character from that reported in this paper. Mallet and Thurston knew nothing about the equilibrium diagram as it stands to-day. Charpy worked with annealed metal and the Alloys Research Committee used worked metal in the investigation.

THE EQUILIBRIUM DIAGRAM

In Fig. 1, is shown the equilibrium diagram. The co-ordinates are temperatures and percentage composition. The upper heavy line A B C D E F G, represents the freezing curve of the molten metal. Between it and the dotted lines crystals and melt co-exist, and below are shown the various phases into which the metal crystallizes. The boundary lines, b_2 b_3, b_1, b_4, c_1, b_4, etc., have been established by annealing cast specimens to equilibrium and quenching at different temperatures. Consequently the positions of these lines may be made to change somewhat, depending somewhat upon the manner of treatment of the metal. If an alloy of 60 per cent copper were quenched at a temperature of 800°, it would consist of pure B-metal; if quenched at some temperature between 470° and 740°, it would consist of A+B crystals, while it would consist of A+B crystals if quenched below 470°.

---

[1] Phil. Mag. 21, 66 (1842).

[2] Thurston: Materials of Engineering. Part 3.

[3] Bulletin de la Société d'Encouragement l'Étude des Alliages.

[4] Proc. Inst. Mech. Engineers, 791 (1905).

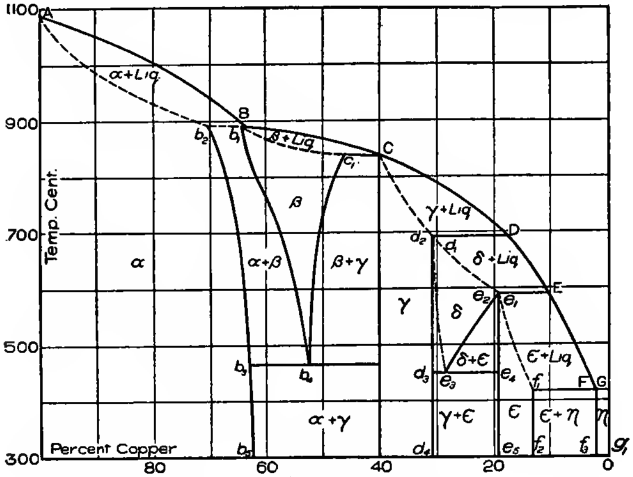

Fig. 1.

MATERIALS AND APPARATUS.

The crucibles used for this work were made from cylinders of Acheson graphite. A small crucible 4 inches in diameter and 6 inches in height (outside dimensions) was used for the melt. This rested in a larger crucible 6 inches in diameter and 8 inches high, which in turn was packed in the electric resistance furnace. This permitted the crucible containing the metal to be removed without tearing out the furnace charge.

The dimensions of the furnace were 34 x 23 x 15 inches. Its capacity was 30 K W. It was built of Queen's Run fire brick and cement. The electrodes were made of Acheson graphite 2 x 4 inches (made up of 2 x 2 inches) and extended inward through the ends of the furnace about 7 inches with 4 inches outside. They were held in place by water-cooled electrode holders.[1] Fig. 2. shows a top view of the furnace. A is the brick wall, B a thick lining of siloxicon to prevent loss of heat by radiation, D the space occupied by granular carbon, C crucibles, E electrodes and F electrode holders. A thin layer of siloxicon was also placed above and below the granular carbon. About 125 volts was used at the beginning of a run. After the furnace became heated this dropped to about 50 volts. A temperature of 1200° could easily be attained in this furnace.

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[1] Gillett. Jour. Phys. Chem. 15, 213 (1911).

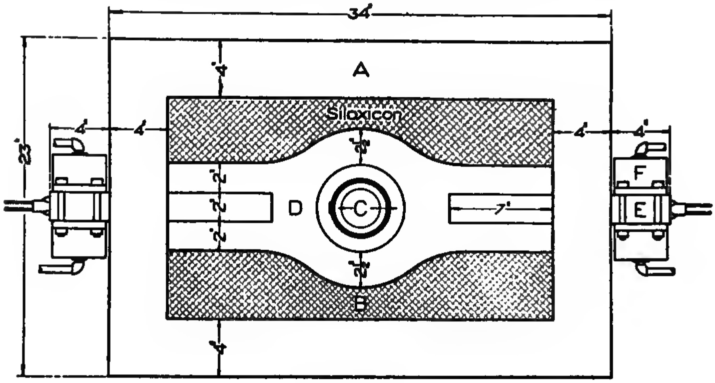

Fig. 2.

The moulds were also made of Acheson graphite. Two slabs 1 x 5 x 17 inches from which the pattern was cut, were clamped together. The pattern consisted of the test piece proper, a riser and a centrifugal sprew. The sprew gave the metal a smooth gentle flow and prevented splashing. It also prevented particles of oxide from being carried into the test-piece.

In order to fill the mould completely it was necessary to incline it at an angle of about ten degrees from the horizontal and to heat it. By inclining it, the molten metal was pushed up the incline, thus forcing out all the air. It was necessary to heat the mold so that the molten metal would not become chilled upon entering it and thus prevent the formation of a perfect test-piece. The heating was done by means of three muffle burners placed vertically in a frame upon which the mould rested. The intensity of the heating varied from below dull redness for the lower melting alloys to bright redness for those melting at higher temperatures.

Oxidation during the melting was cut down by the use of powdered charcoal or sodium chloride, and by passing illuminating gas directly into the crucible through the cover. To prevent the oxide, which formed after the crucible was uncovered for pouring, from being carried along with the melt into the mould, the metal was poured from the bottom of the crucible. A support was arranged so that the crucible could be held stationary, directly over the mould. The pouring was then done through a hole in the bottom of the crucible, by drawing a plug which extended to the top. The mould was held in the proper position by means of adjustable iron guards. The excess metal from the crucible ran over into an asbestos trough and was carried into a vessel of water.

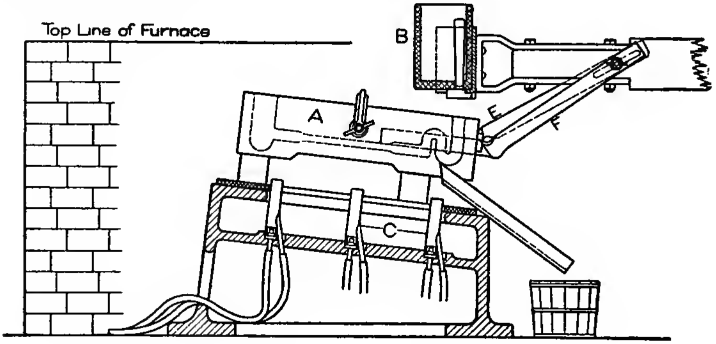

Fig. 3.

The arrangement of the apparatus is shown in Fig. 3. A is the mould resting upon graphite blocks, and held in place by the movable guards E, and F. A section of the crucible B is shown with the hole for pouring directly over the mouth of the mould. C is the frame holding the muffle burners. The castings were all removed from the mould and quenched in water as quickly as possible, in order to decrease the size of the crystals and therefore obtain greater strengths.

Electrolytic copper and pure Bertha spelter were used for the test-pieces. About 1600 grams of metal were used for one charge. In a majority of the pourings, the temperatures were taken. A Hoskins base metal thermo-couple was used.

TESTING

The test-pieces were ten inches in length and 0.40 inch in diameter, with grips at the ends 0.75 inch in diameter. The test section was six inches long. The test-pieces were cast ready for testing, to avoid the necessity of machining.

The diameters of the test sections were taken both before the break and also of the broken ends. From these measurements the tensile strengths based upon the original areas, as well as upon the reduced areas, were computed.

Ductilities were computed from 5 inch lengths on the test sections.

Each piece was analyzed electrolytically for copper, and the zinc content obtained by difference.

Sections of various test-pieces throughout the series were examined microscopically to locate any change in the positions of the boundary curves between the different fields.

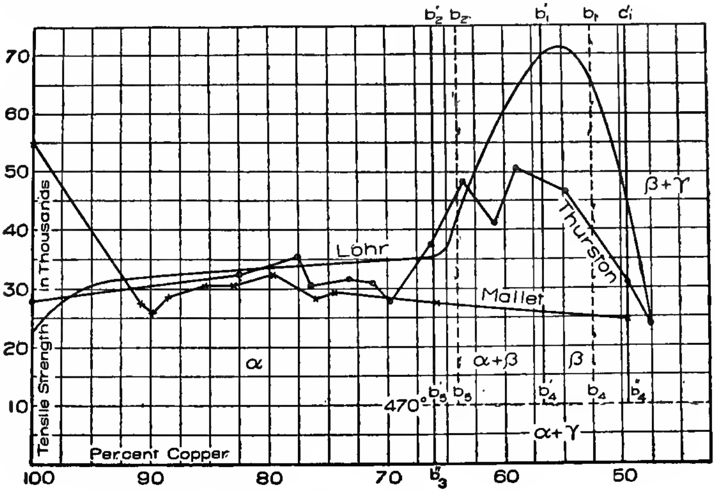

Fig. 4.

RESULTS

The tensile strengths are shown graphically together with those of Mallet and Thurston in Fig. 4. They are platted with percentages of copper against pounds per square inch. Throughout the α-field the tenacity remains almost uniform, increasing a little more than 5000 pounds per square inch. From about 35,000 pounds per square inch at 65 percent copper the strengths increase very rapidly to a maximum of 71,000 pounds per square inch in the β-field at a composition of 55.4 percent copper. From this point to 47.5 percent copper the values drop suddenly to about 24,000 pounds per square inch. On account of the brittleness of the metal, no work was done beyond this point.

Mallet's experiments were done with prisms 0.25 inch square, and included no tests in the field of maximum strength. Thurston's tests were made with test-pieces cast by commercial processes, and not necessarily round in every case. Then, too, they were slow-cooled, and consequently in the region of maximum strength the β metal probably broke down into $\alpha + \gamma$ which is brittle, giving low values.

The microscopic examination showed that the α-phase exists as far as 66 percent copper. The $\alpha + \beta$-phase extends from this point to about 57 percent copper, while the pure β-phase occurs between 57 and 50 percent copper. Comparison with the equilibrium diagram shows that the boundaries are changed somewhat from the positions they occupy under equilibrium conditions. This is due, of course, to the method of rapid cooling employed in this work, whereby the grain size of the metal is reduced and the strength increased, but a condition of equilibrium is not attained before quenching. As was expected, the changes in the tensile strengths of the alloys agree very well with the changes in the internal structure as brought out microscopically. The values remain pretty uniform throughout the α-field and increase very rapidly when the β-phase begins to appear at about 66 percent copper. As the proportion of pure β metal increases, the strength continues to increase until a maximum is reached in the field for pure β. When the brittle γ metal makes its appearance, the tensile strengths decrease rapidly.

In Fig. 5 comparison is made with the work of Charpy on annealed brasses and with that of the Alloys Research Committee (A. R.) on worked metals. As would be expected, the tensile strengths of the worked metal are greater than those of cast metal, due, of course, to decrease in grain size brought about by working the metal. On the other hand all other conditions being equal, annealed brasses should give lower values, than those resulting from castings without heat treatment. This would naturally result from the increase grain size. Therefore, Charpy's high results must undoubtedly be due to the small size of the test-pieces which he used. They were 5 mm in diameter, which is one-fourth the cross section of those in this work. Mallet's abnormally high value for cast copper may also be accounted for in the same manner.

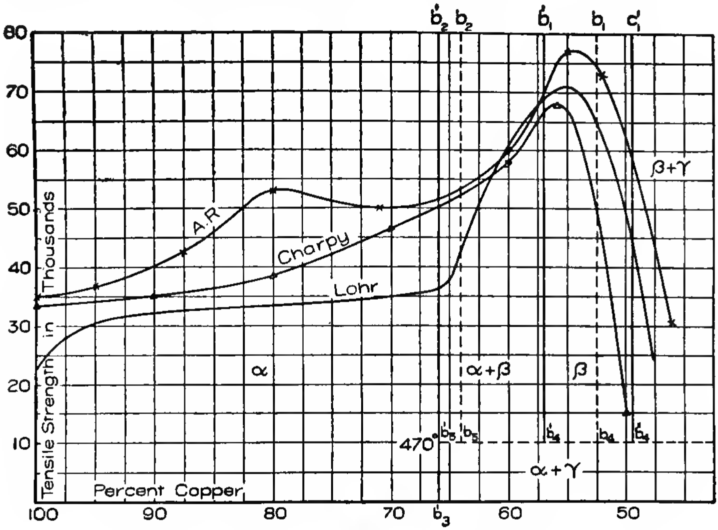

Fig. 5.

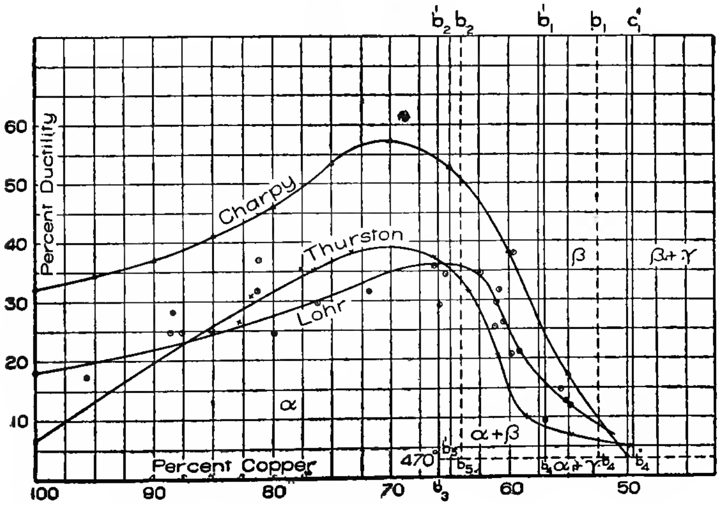

Fig. 6.

Some very high tensile strengths were obtained from the reduced areas of the test-pieces. In many cases they were twice the regular values. The maximum for these values was 135,000 pounds per square inch, with a composition of 60 percent copper. The ductility curve is shown in Fig. 6. This rises gradually with the addition of zinc attaining a maximum of 36 percent at about 65 percent copper. It then drops suddenly, and gradually falls off to almost zero.

The best results were obtained by pouring the metal at temperatures within the range between 100° and 200° above the freezing curve or liquidus.

CONCLUSIONS

The following conclusions may be drawn from the results of this work:

1. A study of the tensile strengths of the brasses containing 47.5 to 100 percent copper has been made.
2. The X brasses give almost a constant value for the tensile strengths.
3. The maximum tensile strength occurs in the neighborhood of a 55 percent copper alloy, and its value is about 71,000 pounds per square inch.
4. The B alloys give the highest tensile strength.
5. The maximum strength does not occur on a boundary curve.
6. The variations in the tensile strength agree very closely with the constitution of the alloys, as checked up by the microscope.
7. A tensile strength of 137,000 pounds per square inch, as taken from the fractured ends, has been obtained.
8. A maximum ductility of about 36 percent elongation has been regularly obtained. One piece, however, showed an elongation of 60.4 percent, but could not be duplicated.
9. It is possible to obtain a cast brass having an ultimate tensile strength of 71,000 pounds per square inch, and an ultimate elongation of 14.8 percent; or, a brass having an ultimate tensile strength of over 36,000 pounds per square inch and an ultimate elongation of 35.6 percent.
10. A method for continuous pouring of metal has been devised.
11. The effect of temperature of pouring has been investigated.

EXTRACTION OF THORIA

By Charles Baskerville

College of City of N. Y., New York City, N. Y.

Thorium dioxide is obtained in the main from monazite sands, which, in round numbers, may be said to have this composition:—

P_2O_5 (phosphates)	29 per cent.
Ce_2O_3 (earths)	31 per cent.
Di_2O_3 (earths)	31 per cent.
SiO_2 (silicates)	1.50 per cent.
ThO_2 (silicates and perhaps phosphates)	6.50 per cent.

In the winning it is necessary to get rid of the phosphorus compounds as they materially interfere with the efficiency of the thoria when used for mantles. This is usually accomplished by converting the earths into insoluble oxalates after solution of the sand. Other methods have been proposed and some are now used commercially for avoiding this by fusion with alkaline carbonates and leaching the phosphates out with water, dissolving the residue in suitable acids, and then making the separation of the earths.

Troost[1] prepared thorium carbide (ThC_2) by heating the oxide with carbon. Moissan and Etard[2] made elaborate studies on the formation and properties of thorium carbide. Muthmann, Hofer and Weiss[3] fused monazite sand with carbon and dissolved the carbides and phosphides obtained in hydrochloric acid. Whereas the objectionable phosphoric compounds are removed in this manner, other practical difficulties arise, one being the hardness of the product which involves expense in grinding the fused product.

The work of Kress and Metzger[4] indicates that thorium does not occur as the silicate in monazite. It is a fact, however, that silica or silicate is a constant, but variable, constituent of the sand and must be taken care of, whatever means of extraction is applied. When the carbides are made by electric fusion of the sand with carbon some silicon carbide is produced which cuts the grinding machinery in the later process of pulverizing. We have found that the addition of a small amount of fluorspar reduces this difficulty, yet the expense of some grinding remains.

---

[1] Compt. rend., 1893, **116**, 1227.

[2] Ann. chim. phys., 1896, (VII), **9**, 302; and 1897, (VII), **12**, 427; Compt. rend., 1896, **122**, 573 and 1462.

[3] Ann., 1901, **320**, 260; German Patent 129,416, Aug., 1901.

[4] J. Am. Chem. Soc., 1909, **31**, 640.

In order to reduce this expense to a minimum, I decided to deliberately produce calcium carbide within the mass, which, when thrown into water, would disintegrate.[1] Although Moissan has shown that thorium and the rare earth (?) carbides are attacked by water, the speed of the reaction is very much less than with calcium carbide and is also much dependent upon the fineness of the particles. Hence comparatively little of the thorium and rare earth (?) carbides would be decomposed by such treatment. Many experiments were carried out, with theoretical and practical mixtures, in various types of furnaces (Stokem, Moissan, Heroult, and resistance) with direct and alternating currents. The numerous experimental details[2] need not be recited. Suffice it to say that a satisfactory charge may be had with a sand of the approximate composition given above as follows:

Monazite sand	1.0 lb.
Carbon (Petroleum coke)	1.10 lb.
Lime	0.80 lb.
Fluorspar	0.15 lb.

The best results were obtained with such charges by using a current of 35 volts and 125 amperes for one and one-half hours.

The procedure is as follows:

The mixture (unground sand being used) is made according to the principles outlined above, and then subjected to electric heat until phosphorus ceases to come off.[3] The mass is allowed to cool and then to decompose slowly by exposure to the air or quickly by placing in water. In the latter case the acetylene may be utilized, the mass falling to a fine powder. The dissolved and suspended calcium hydroxide are removed by washing. The residue is treated with hydrochloric acid and the thorium separated from the solution by sodium thiosulphate or other methods. The process is controlled by the Welsbach Light Co., of Gloucester City, N. J., and is published with their consent and approval.

---

[1] Application for letters patent on this method of disintegration of fused masses has been made.

[2] The experimental work was done by Mr. S. G. Warner of my staff.

[3] This phosphorus may be condensed.

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.—THE ANALYSIS OF PHOSPHORUS TRICHLORIDE

By Gregory Paul Baxter and Charles James Moore
Harvard University, Cambridge, Mass.

In two recent investigations in this laboratory trisilver phosphate[1] and phosphorus tribromide[2] have been analyzed with the following results for the atomic weight of phosphorus:

		Ag = 107.88	Ag = 107.87	Ag = 107.86
Ag_3PO_4	P =	31.04	31.03	31.02
PBr_3	P =	31.027	31.024	31.021

While the agreement between the values yielded by the two researches is reasonably close, yet because of the low percentage of phosphorus in both compounds, 7.7 and 11.5 respectively, and the consequent magnification of the percentage experimental error in calculating the atomic weight of phosphorus, the subject has been further investigated by the analysis of phosphorus trichloride. This substance contains a higher percentage of phosphorus than either the phosphate or tribromide, 22.6, and might be expected therefore to yield results of fully as much value as those given by the other two compounds.

Silver phosphate and phosphorus tribromide are compounds of so different character, containing phosphorus in two states of valence, and the analytical processes were so different, that there is little probability that both methods were affected by constant errors to the same extent. Yet any uncertainty of this sort would be further removed if still a third method is found to be in accord with the first two.

The method of preparing and analyzing phosphorus trichloride was very similar to the one previously employed with the tribromide. Phosphorus trichloride was synthesized from pure dry phosphorus and a very slight excess of pure dry chlorine in a vacuum. The product was freed from the less volatile pentachloride by fractional distillation in a vacuum. A series of fractions was then collected and analyzed for chlorine in the usual way, after decomposition with water and oxidation of the phosphorous acid produced.

---

[1] Baxter and Jones, Proc. Am. Acad., **45**, 137 (1910); Journ. Amer. Chem. Soc., **32**, 268; Zeit. anorg. Chem., **66**, 97.

[2] Baxter, Moore and Boylston, Proc. Am. Acad., **47**, 385 (1912) Journ. Amer. Chem. Soc., **34**, 259; Zeit. anorg. Chem. **74**, 365.

PURIFICATION OF MATERIALS

Water.—All the water used in this research was prepared from the laboratory supply of distilled water by further distillation, first from an alkaline permanganate solution, and then a second time, after the addition of a trace of sulphuric acid, through a block tin condenser. No rubber or cork was used in the connection between the condenser tube and the Jena glass still.

Ammonia.—The best commercial ammonia was distilled into the purest water.

Nitric acid.—C. P. concentrated acid was distilled through a platinum condenser, with rejection of the first two thirds of the distillate. It was always carefully tested in a nephelometer for traces of halogens.

Chlorine.—This substance was prepared by warming C. P. concentrated hydrochloric acid with granulated manganese dioxide. In order to remove hydrochloric acid, the gas was scrubbed with water in two large gas washing bottles and two towers filled with moist glass pearls. Drying took place in two towers filled with glass pearls drenched with concentrated sulphuric acid and a long tube filled with resublimed phosphorus pentoxide. Finally the gas was condensed to the liquid state in a bulb cooled to a temperature of about —78° by immersion in a bath of solid carbon dioxide and alcohol. The preparation and purification of the chlorine took place in an apparatus constructed wholly of glass, with ground stoppers and connections throughout.

On account of the ready action of moisture on the halides of phosphorus it was particularly necessary to dry the chlorine as completely as possible. Hydrochloric acid also was undesirable, since its elimination from the trichloride by distillation would be somewhat uncertain. Air and carbon dioxide were of lesser importance. However, the air at any rate must have been largely removed during the liquefaction of the gas.

Phosphorus. As in the previous research, phosphorus was purified by distillation with steam at atmospheric pressure in an apparatus constructed wholly of glass. The purified material was preserved under water until used. Similar phosphorus was found in the earlier work to be essentially free from arsenic.[1] The material used in the synthesis of the first series of fractions of phosphorus trichloride was once distilled, that used in the second twice.

Silver. The same preparation of silver was used here that was employed in the tribromide analyses. The method of purification consisted in double precipitation as chloride, precipitation as metal by ammonium formate, and electrolytic deposition. The electrolytic crystals were fused in a current of hydrogen on a boat of pure lime, and finally, after cleansing with nitric acid, the buttons were dried in a vacuum at about 400°.

Hydrogen Peroxide. Merck's "Perhydrol," containing 30 per cent. hydrogen peroxide, was found to be free from sulphuric acid and halogens and to leave no residue upon evaporation. Hence it was employed without further treatment.

Nitrogen. Atmospheric nitrogen free from oxygen was obtained by Wanklyn's well-known method of passing air through very concentrated ammonia solution, and then over hot copper gauze in a hard glass tube. The excess of ammonia was removed by scrubbing with a dilute solution of sulphuric acid in three large gas-washing bottles. Since hydrogen is formed by the catalytic decomposition of a portion of the excess of ammonia, this impurity was oxidized in a hard glass tube filled with red hot copper oxide, and the gas was then dried in six towers filled with beads drenched with concentrated sulphuric acid and in a long tube filled with resublimed phosphorus pentoxide. Finally the gas was passed through a third hard glass tube filled with hot copper to combine with any last trace of oxygen. The apparatus in which these operations were carried out was constructed entirely of glass with ground glass connections throughout.

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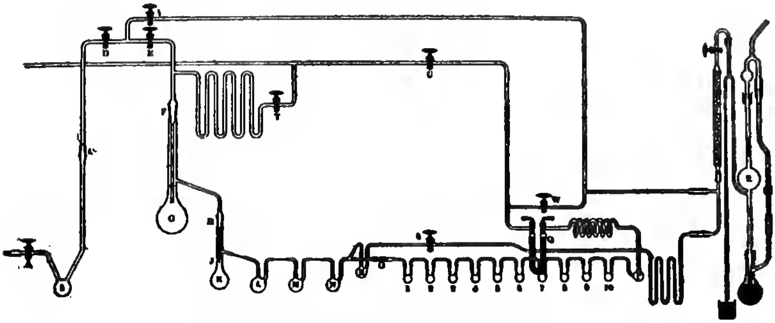
[1] Proc. Amer. Acad., **47**, 587 (1912); Journ. Amer. Chem. Soc., **34**, 259; Zeit. anorg. Chem., **74**, 365.

THE PREPARATION OF PHOSPHORUS TRICHLORIDE

Although the phosphorus trichloride was made in the same way as the tribromide, by allowing a slight excess of pure dry chlorine to react with pure dry phosphorus in a vacuum, the problem of freeing the trichloride from pentachloride differed somewhat from the preparation of the tribromide free from pentabromide. When the tribromide is distilled, even in a vacuum, any pentabromide present is largely dissociated into tribromide and bromine so that the excess of bromine may be removed with the first fractions by distillation. With the pentachloride, however, the dissociation is very much less at the same temperature and since the trichloride boils nearly one hundred degrees lower at atmospheric pressure than the tribromide, the conditions were far less favorable for the elimination of pentachloride by decomposition. On the other hand the inappreciable dissociation of the pentachloride at room temperatures and the slight volatility of this substance facilitates the separation of the tri- and pentachloride by simple fractional distillation, for the pentachloride accompanies the relatively very volatile trichloride to only a barely perceptible extent.

The synthesis of the trichloride was effected in an apparatus constructed entirely of glass, shown in the figure on page 25. About 25 grams of phosphorus were freed as completely as possible from water by cooling and pressing between the folds of hardened filter paper. Then it was weighed to a centigram and placed in the distilling flask G, which had previously been filled with nitrogen through the stopcock T. The flask was fitted to the well-ground and polished joint F, but it was not connected to the remainder of the apparatus at H, and the constricted tube J opened into the air.

In order to dry the phosphorus completely, the flask was surrounded with boiling water and for four hours a slow current of pure dry nitrogen was forced in at T and flowed out at the end of the constricted tube J. The melted phosphorus was agitated from time to time by shaking the flask in order to liberate any steam which might have been mechanically entangled and to bring new material to the surface of the phosphorus. During this operation a portion of the phosphorus distilled into the cool tube J, and a small amount was vaporized into the air. Probably, too, small amounts of acids of phosphorus were produced since slight oxidation of the phosphorus necessarily took place while it was being introduced into the flask. As soon as the phosphorus had been dried in this way, the end of the constricted tube J was sealed, the stopcock T was closed and the flask, after being cooled, was exhausted as completely as possible through the stopcocks E and V by means of the Topler pump X. All the ground glass joints were made gas tight by means of a minimum quantity of syrupy phosphoric acid, and outside this, to prevent the absorption of moisture, soft paraffin was smeared.



Phosphorus Trichloride Apparatus

In the meantime the bulb B was being filled with liquid chlorine in the fashion already described. A considerable excess of this substance was collected at first. The bulb was then suspended on a balance and the excess of chlorine was allowed to evaporate. When the weight of the residual chlorine was 0.3–0.4 gram larger than the amount theoretically equivalent to the phosphorus, the bulb was again plunged into the alcohol-carbon dioxide bath to check the evaporation. Next the bulb B was connected with the remainder of the apparatus by the joint C. The stopcock A was closed and the bulb B was still further cooled with liquid air. At this temperature, the chlorine not only becomes solid but its vapor pressure becomes so low that when the bulb B was exhausted through the stopcocks B and V, while E remained closed, the mercury of the pump showed no signs of attack.

The stopcock V was now closed and E was opened so as to establish communication between the bulbs B and the flask G. Then the liquid air bath was removed from B and the chlorine was allowed to absorb heat slowly, but by occasional immersion in alcohol and carbon dioxide the temperature of the chlorine was prevented from exceeding —40°. At first the phosphorus was only slowly affected by the chlorine but once the reaction was started by warming the phosphorus gently, it progressed rapidly to completion; so rapidly in fact, that it was necessary to cool the flask G with water in order to prevent rapid volatilization of the trichloride formed. While the reaction was progressing, a large amount of the while solid pentachloride formed on the walls of the flask, but at the end of the synthesis this pentachloride was dissolved in the liquid trichloride by gently shaking and warming the flask nearly to the boiling point of the trichloride at atmospheric pressure. The unchanged phosphorus still remaining then was able to convert the greater part of this pentachloride to trichloride. The flask was filled with nitrogen and allowed to stand over night.

The next morning the flask and its contents were cooled with solid carbon dioxide and alcohol, and nitrogen was admitted through T until the internal pressure was greater than atmospheric. Then the end of the constricted tube J was cut off, and the remainder of the apparatus, which had previously been filled with nitrogen, was attached by the joint H. Next the bulbs G, K, L, M, N, and R were exhausted through S, while stopcocks D, E, T, V, and W were closed. In order to prevent access of chlorine or phosphorus trichloride to the pump, the bulb R was immersed in liquid air. The pump was further protected by a tube containing solid potassium hydroxide.

During the fractional distillation of the trichloride, the bulbs 1 to 10, in which the final fractions of trichloride were to be collected, were protected from contact with the first fractions. This was effected by maintaining nitrogen at atmospheric pressure beyond the valve O. This valve was very well ground and polished so as to be nearly gas tight without any lubricant. The very slight leakage which occurred produced a slow reverse current of nitrogen through the valve into the pump by way of the bulb R.

Under as low a pressure as could be maintained by the pump the trichloride was distilled from G to K by warming G to about 15° and cooling K to —78°. When about four-fifths of the trichloride had been distilled into K, this bulb was warmed to 15° while L was cooled to —78°. Again four-fifths of the trichloride in K was collected in L. At this point K was cooled and the capillary between K and L was sealed. In this way the residues of the first two distillations were cut off completely from the rest of the apparatus. It is certain that the trichloride originally contained pentachloride because a white incrustation appeared on the sides of G toward the end of the first distillation. The distillation was continued from L to M and from N to M, the last fifth being rejected in each distillation by sealing off the containing flask. Thus the greater part of the less volatile pentachloride was eliminated. Next, in order to expel the more volatile impurities such as hydrochloric acid, if present at all, about one-quarter of the remainder was distilled into the bulb R and this bulb was then cut off by sealing the capillary.

The purification of the trichloride was now considered complete, so that the next step consisted in filling the numbered bulbs by distillation. The bulb N was cooled to —78°, the bulb P was immersed in liquid air to protect the pump and the train of bulbs was exhausted through the U-tube Q, containing resublimed phosphorus pentoxide, and the stopcock W. The valve O, inside which a piece of soft iron had originally been sealed, could now be pulled from its seat by means of a magnet. When the remaining system had been exhausted as completely as possible, the right hand capillary of the bulb 10 was sealed. The weighing bulbs were now filled in order beginning with 10, by warming the bulb N to 15° and cooling the bulbs in turn to —78°. Each of the numbered bulbs was about four-fifths filled with trichloride. As soon as four bulbs had been filled they were sealed off as a unit, and the next four to be filled were treated in the same way. Finally, while the trichloride was still cold, each individual bulb was sealed off at the capillaries. Great care was taken in sealing the capillaries to avoid decomposition of the trichloride by unnecessary heating. There never was any sign of decomposition of the trichloride during the process.

The trichloride was a colorless highly refractive liquid which gave every outward evidence of purity, and showed no change in appearance on long standing. One of the rejected residues was left in the sunlight for several months without showing any sign of decomposition.

Two series of fractions of phosphorus trichloride were prepared. In the first series only light bulbs were available for collecting the material, and as more than enough trichloride to fill all these bulbs was contained in N. the residue from the distillation could not be analyzed. Furthermore in this first preparation the bulbs K, L and M contained tiny crystals of electrolytic silver. This was introduced to assist in the elimination of the pentachloride by combining with the chlorine, but as it seemed in practice to serve no useful purpose, it was omitted in making the second preparation. In the second experiment, however, twelve bulbs were actually available and the material in N was sufficient only to fill ten. As soon as the last nine had been filled, instead of distilling the residue into the third bulb, it was distilled into the second. When all the trichloride has disappeared from N a slight white solid residue appeared, showing that in spite of all precautions, a trace of pentachloride had accompanied the trichloride even in the fourth distillation. Since it seemed probable that the last fraction contained pentachloride, it was again distilled from bulb 2 into bulb 3, a small residue being rejected.

THE DETERMINATION OF THE WEIGHT OF THE TRICHLORIDE AND ITS ANALYSIS

The analysis of the trichloride followed very closely the procedure employed with the tribromide. First the trichloride was decomposed with water, then, on account of the reducing effect of phosphorus acid on silver salts, the phosphorus acid was oxidized with hydrogen peroxide and nitric acid. Finally the chloride was precipitated with a weighed equivalent amount of pure silver and the silver chloride was weighed. Since the determination of the weight of trichloride and its analysis are very intimately connected, they are described together.

The weight of the trichloride was found in each analysis by weighing the bulb with its contents and then, after breaking the bulb, collecting and weighing the glass. The bulb was first carefully cleaned on the outside and dried, and left in a desiccator over sulphuric acid for at least twenty-four hours. Its weight in air was then found by substituting standardized weights for the bulb on the balance. The buoyant effect of the air was estimated by finding the volume of the bulb in the usual way from the loss in weight under water of known temperature. The conditions of the atmosphere were taken into account in calculating the buoyant effect of the air on the bulbs and weights. Since the bulb was exhausted when sealed no correction is necessary for the space in the bulb not filled with liquid.

After the bulb had been weighed and its volume determined, it was placed in a 1000 cc. thick-walled Erlenmeyer flask together with somewhat over 200 cc. of redistilled ammonia and 10 cc. of pure 30 per cent. hydrogen dioxide. The flask was warmed to about 60°, then, after a glass stopper which had been carefully ground into the neck of the flask had been inserted, and the flask cooled to 0°, it was shaken violently enough to break the bulb. The heavy trichloride reacted quietly at the bottom of the aqueous solution, until at the end of five minutes decomposition was complete. The flask was then allowed to stand twenty-four hours, with occasional shaking. This long standing was necessary to allow a small quantity of ammonium chloride fumes to be collected in the aqueous solution. The precaution of cooling to 0° was found advisable because the reaction was too violent at room temperature.

The flask, cooled to produce inward pressure, was next carefully opened and the solution was filtered into a three-liter ground stoppered precipitating flask, while the particles of glass were collected upon a small filter paper. This paper was very thoroughly rinsed with pure water until the filtrate and washings amounted to about 1200 cc.

In order to find the weight of the glass the filter was burned at as low a temperature as possible in a weighed platinum crucible. When the weight of the glass, corrected to vacuum, was subtracted from the corrected weight of the bulb and the trichloride, the weight of the trichloride in vacuum was obtained. In the investigation upon the tribromide it was shown by several blank experiments that this method of collecting the glass and finding the weight of the trichloride is a satisfactory one.

The filtrate containing ammonium chloride was next acidified by the addition of about 40 cc. of concentrated nitric acid which had been diluted to about 300 cc. In order to avoid possible loss of chlorine, the acid was poured into the solution through a thistle tube, the stem of which extended to the bottom of the flask. Thus, any chlorine locally set free by the nitric acid was reduced by the phosphorus acid still remaining. There was, however, never any evidence that chlorine was set free even locally by the nitric acid.

The solution was allowed to stand for 48 hours before precipitation, in order to allow the oxidation of the phosphorous acid to become as nearly as possible complete, because in the tribromide work this delay was found advisable.

A quantity of silver equivalent to the trichloride within a very few tenths of a milligram was weighed out and dissolved in nitric acid in a flask fitted with a column of bulbs to prevent loss of material by spattering. After the silver solution had been freed from oxides of nitrogen by dilution and heating, about 40 cc. of concentrated nitric acid were added and the whole was diluted to a volume of about one liter. The silver solution was then quantitatively added to the chloride solution with constant agitation, and the stoppered precipitating flask was allowed to stand for several days with occasional shaking. Then the solution was cooled to 0° to lower the solubility of the silver chloride and again allowed to stand until the precipitate had coagulated and settled so completely that the supernatant liquid was apparently clear. Portions of the solution were then tested in a nephelometer[1] for excess of chloride or silver. As a matter of fact, chloride was always found in slight excess. The deficiency of silver, which was never more than a few tenths of a milligram, was made up as nearly as could be estimated by means of a hundredth normal solution of silver nitrate. After thorough shaking and standing until the solution was clear, tests for excess of chloride or silver were again made. If necessary, this process was repeated, until eventually the amounts of chloride and silver were equivalent.

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[1] Richards and Wells, Am. Chem. J., **31**, 235 (1904); **35**, 510 (1906).

The solution was now allowed to stand for a week with occasional shaking and then was tested again in the nephelometer. In a few cases a deficiency of one or two-tenths of a milligram of silver was found, owing apparently to extraction of occluded soluble chloride from the silver chloride. This deficiency of silver was supplied and the solution was left for another week before being tested again, and the process was repeated until in the course of a week no further change in the solution took place. In a few analyses the solutions were tested over a period of eight weeks but in no case was any appreciable change in the end point found after it had remained constant for a week. In most cases the final end point was reached within two weeks.

In a number of analyses both the chloride and silver solutions were cooled to 0° before precipitation. This procedure had no perceptible effect on the result, nor did it seem to lengthen appreciably the period necessary for reaching a permanent end point.

Less difficulty was experienced from occlusion by the silver chloride in this research than by the silver bromide in the previous one. The amount of occluded substance seemed to be smaller and the time required for equilibrium to be reached was less. This is probably due to the greater solubility of the chloride.

As soon as a permanent end point has been reached in an analysis, the silver chloride was collected and determined. Owing to the fact that silver chloride is many times as soluble as silver bromide, more difficulty was experienced in finding a suitable method for its determination, and the first series of analyses were sacrificed in unsuccessful experiments.

It was an easy matter to collect the precipitate itself upon a Gooch-Munroe-Neubauer crucible, and to determine its weight after drying it at 190° for some hours. Residual moisture was found by fusing the main bulk of the precipitate and determining the loss in weight. The latter was never as much as 0.006 per cent. the weight of the salt.

The difficulty lay in finding the silver chloride dissolved in the filtrate and washings. In Analyses 16 and 17, after filtration of the ice-cold mother liquor, the precipitate was washed and transferred to the crucible with ice cold water. The filtrate and washings, amounting to about four liters, were evaporated to very small bulk, until the excess of nitric acid has been expelled. After dilution and filtration, the silver was deposited electrolytically in a small platinum dish. When deposition was complete the electrolyte was displaced by water while the current was still running. The film of silver was then dissolved in nitric acid and the silver precipitated as silver iodide. The precipitate was collected on a small Gooch-Munroe-Neubauer crucible and weighed.

The filter used for the filtration of the mother liquor before electrolysis was incinerated and after the ash had been treated with nitric acid, the solution was added to the solution of the electrolytic film. The mother liquor of the electrolysis was saturated with pure hydrogen sulphide gas and the precipitate, chiefly sulphur, was found, after incineration of the paper, to be free from silver.

Because this process was a long and tedious one, the experiment was tried of reducing the solubility of the silver chloride by means of an excess of silver nitrate and partially washing the precipitate with a similar solution. This method is the usual one in treating silver halides for quantitative purposes, but it was not attempted here at first because, in the phosphorus tribromide work, even a slight excess of silver was found to be partially reduced by unoxidized phosphorus acid.

To our great satisfaction this method was successful. The silver chloride precipitate was perfectly white both before and after the addition of the silver nitrate and remained so during all the subsequent steps.

When the end point had been reached, an excess of about 0.1 gram of silver nitrate in solution together with considerable nitric acid was added to the analysis. The flask was shaken and packed in ice, where it was left, with occasional shaking, for a day. The clear solution was then passed through the crucible and the precipitate was washed three times with a solution of silver nitrate containing 0.05 gram per liter, and once with pure water. The filtrate and these four washings were discarded and a correction of 0.00001 gram per liter was applied for dissolved silver chloride.

Richards and Wells[1] found the solubility of silver chloride in dilute hydrochloric acid at room temperature to be 0.00003 gram per liter, but as Richards and Willard[2] found the solubility in water at 0° to be about one sixth that at 25°, the above estimate seems to be a liberal one for the solubility as 0° in dilute silver nitrate. The precipitate was then further washed with pure water eight to ten times and transferred to the crucible.

The silver chloride dissolved in the wash waters was carefully determined by comparison with standard silver solutions in a nephelometer. The unknown and the standard solutions were both treated with an excess of ammonia and then an excess of nitric acid, after the addition of an excess of silver solution, and the two tubes were treated in as nearly as possible an identical fashion.

The precipitating flask was rinsed with ammonia, and, if the solution was found to contain silver, the quantity was determined in a similar fashion in the nephelometer and a correction applied.

The following tables contain the results of all the analyses which met with no accidents.

Weighings were made on a No. 10 Troemner balance sensitive to a very few hundredths of a milligram, while the gold-plated weights were carefully standardized to hundredths of a milligram by the method described by Richards.[3]

Vacuum corrections were applied as follows:

	Specific gravity	Vacuum correction
Weights	8.3	+ 0.000145
AgCl	5.56	+ 0.000071
Ag	10.49	— 0.000030
Glass	2.5	+ 0.000335

In the calculation the atomic weight of silver is assumed to be 107,880 and that of chlorine 35,457.

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[1] Pub. Car. Inst., No. 28 (1905); Jour. Amer. Chem. Soc., **27**, 459; Zeit. anorg. Chem., **47**, 56.

[2] Pub. Car. Inst., No. 125 (1910); Jour. Amer. Chem. Soc., **32**, 4; Zeit. anorg. Chem., **66**, 229.

[3] Journ. Am. Chem. Soc., **22**, 144, (1900).

Series I. PCl_3: 3 Ag

No. of Analysis	Fraction of PCl_3	Weight of PCl_3 in vacuum grams	Weight of Ag in vacuum grams	Deficiency of Ag gram	Corrected weight of Ag in vacuum grams	Ratio PCl_3: 3 Ag	Atomic weight of Phosphorus
1	1	3,60897	8,50038	0.00110	8,50148	0.424511	31,018
2	8	3,49255	8,22664	0.00070	8,22734	0.424505	31,016
3	4	3,80549	8,96377	0.00050	8,96427	0.424517	31,020
4	5	4,64502	10,94182	0.00030	10,94212	0.424508	31,017
5	2	3,99011	9,39923	0.00020	9,39943	0.424505	31,016
6	7	3,38036	7,96291	0.00010	7,96301	0.424508	31,017
	Average					0.424509	31,017

Series II. PCl_3: 3 Ag

7	3	4,59507	10,82411	0.00030	10,82441	0.424510	31,017
8	10	4,40117	10,36751	0.00020	10,36771	0.424508	31,016
9	4	5,71561	13,46368	0.00040	13,46408	0.424508	31,017
10	9	5,18668	12,21784	0.00030	12,21814	0.424506	31,016
11	5	5,15583	12,14525	0.00030	12,14555	0.424504	31,015
12	8	5,13108	12,08685	0.00040	12,08725	0.424504	31,015
13	1	4,85457	11,43585	0.00000	11,43585	0.424505	31,016
14	2	3,58844	8,45324	0.00000	8,45324	0.424505	31,016
15	6	5,91915	13,94317	0.00060	13,94377	0.424502	31,015
	Average					0.424506	31,016

Series III. PCl_3: 3 AgCl

No. of Analysis	Fraction of PCl_3	Weight of PCl_3 in vacuum grams	Weight of AgCl in vacuum grams	Loss on Fusion gram	AgCl from Filtrate and Washings gram	Corrected weight of AgCl in Vacuum grams	Ratio PCl_3: AgCl	Atomic weight of Phosphorus
16	3	4,59507	14,37888	0.00061	0.00291	14,38118	0.319520	31,026
17	10	4,40117	13,77320	0.00046	0.00220	13,77494	0.319506	31,020
18	4	5,71561	17,88965	0.00096	0.00064	17,88933	0.319506	31,020
19	9	5,18668	16,23441	0.00085	0.00074	16,23430	0.319489	31,019
20	5	5,15583	16,13756	0.00095	0.00066	16,13727	0.319498	31,017
21	8	5,13108	16,05934	0.00054	0.00082	16,05962	0.319502	31,018
22	1	4,85457	15,19201	0.00054	0.00098	15,19245	0.319538	31,034
23	2	3,58844	11,23055	0.00054	0.00090	11,23091	0.319515	31,024
24	6	5,91915	18,52577	0.00077	0.00092	18,52592	0.319506	31,020
	Average						0.319509	31,022

The chief point of interest to determine in the examination of the foregoing results is whether the material really represents pure phosphorus trichloride. Judging from the agreement of the results obtained with the different fractions in each series, the material was as uniform as could possibly be expected. While evidence was obtained that the pentachloride is to a very slight extent carried into the trichloride distillate either as such or in the form of its dissociation products, the amount thus accompanying the trichloride diminishes very rapidly with successive distillations. Of course it is possible that a constant boiling mixture of tri- and pentachloride exists, but such a possibility is somewhat remote. If the trichloride actually contained a trace of pentachloride, it would account for the fact that the average result of this research, 31.018, is very slightly lower than that of the tribromide. It is worth noting, however, that five out of thirty-one analyses of the tribromide are as low as the average of the trichloride analyses, and that three of the six series of tribromide analyses yield averages of 31.022, a value only 0.004 higher than the trichloride average. A difference no larger than this is extremely difficult to detect even where the substances analyzed are ideal for the purpose.

The three compounds of phosphorus analyzed, then, yield the following results:

	Ag = 107.880	Ag = 107.870	Ag = 107.860
Ag_3PO_4	31.04	31.03	31.02
PBr_3	31.027	31.024	31.021
PCl_3	31.027	31.015	31.012
Averages	31.028	31.023	31.018

On the whole the tribromide and trichloride may be expected to yield somewhat more certain results than silver phosphate, and the averages of these, given below, are therefore to be preferred.

Ag = 107.880	Ag = 107.870	Ag = 107.860
P = 31.023	P = 31.020	P = 31.017

On any basis the rounded off value 31.02 is fully as exact as the experimental work warrants.

SUMMARY OF RESULTS

1. Methods are described for the preparation of pure phosphorus trichloride and its analysis.

2. The molecular weight of phosphorus trichloride referred to silver 107.880 is found to be 137.389, whence phosphorus has the atomic weight 31.018.

3. Using the same value for silver, the average result of the analyses of silver phosphate, phosphorus tribromide and phosphorus trichloride is 31.028, while the average of the more reliable tribromide and trichloride analyses is 31,023.

We are particularly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in carrying out this investigation.

A REVISION OF THE ATOMIC WEIGHT OF IRON

Fifth Paper — The Analysis of Ferric Oxide

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The atomic weight of iron has already been subjected to three separate investigations in this laboratory. Richards and Baxter[1] first analyzed ferric oxide by reduction in hydrogen, and obtained the result 55.88, a value much lower than the one in general use at that time, 56.02. The problem was further investigated by Baxter[2] by the analysis of ferrous bromide, and the result yielded by material known to be slightly impure, 55.845 (Ag = 107.88) agrees very closely with that obtained by Baxter, Thorvaldson, and Cobb[3] in a very recent investigation with much purer material, 55.838. Furthermore Baxter and Thorvaldson[4] found that meteoric material is identical, so far as could be told by the analysis of ferrous bromide, with material of terrestrial origin.

Thus, although the analysis of ferrous bromide supports the verdict of the oxide analysis in yielding a low value for the atomic weight of iron, yet the difference between the results of the two methods, 0.04, is much too large to be allowed to rest without further investigation. The recent availability of fused quartz apparatus seemed to offer distinct possibilities of improvement in the original oxide analysis, especially in the reduction of the oxide, so that the decision was made to repeat the analysis of ferric oxide with all possible precautions in the light of experience gained since the earlier work.

In outline the operations consisted in preparing ferric oxide by igniting in a current of pure air carefully purified ferric oxide.

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[1] Proc. Amer. Acad., **35**, 253 (1900); Zeit. anorg. Chem., **23**, 245.

[2] Proc. Amer. Acad., **39**, 245 (1903); Zeit. anorg. Chem., **38**, 232.

[3] Jour. Amer. Chem. Soc., **33**, 319 (1911); Zeit. anorg. Chem., **70**, 325.

[4] Jour. Amer. Chem. Soc., **33**, 337 (1911); Zeit. anorg. Chem., **70**, 348.

The oxide was next weighed, and then, after reduction in a current of very pure hydrogen, the weight of the residual metal was found. The problems involved were, therefore, first, the purification of ferric nitrate; second, the preparation of ferric oxide free from higher or lower oxides and occluded gases; third, the complete reduction of the oxide.

PURIFICATION OF REAGENTS

Water. In the earlier stages of the purification of the iron salts, the ordinary distilled water was employed. In the later steps this water was twice redistilled, first from an alkaline permanganate solution, then, after the addition of a trace of sulphuric acid, through a block tin condenser, in an apparatus free from rubber or cork. Usually the distillate was collected in platinum vessels.

Ammonia. The best commercial ammonia was distilled into the purest water in an apparatus constructed entirely of glass.

Nitric Acid. C.P. concentrated acid was distilled from a glass still through a platinum condenser, with rejection of the first two-thirds of the distillate. A platinum receiver also was employed.

Hydrochloric Acid. C.P. concentrated acid was diluted with an equal volume of water and distilled through a glass condenser with rejection of the first half of the distillate.

Sulphuric Acid. C.P. concentrated sulphuric acid was distilled from a small non-tubulated glass retort into a Jena glass flask. Here also the first half of the distillate was rejected.

Oxalic Acid and Ammonium Oxalate. The best commercial substances were three times crystallized in Jena vessels with centrifugal drainage and washing.

Air. Air was freed from organic matter by being passed over red hot copper oxide in a hard glass tube heated electrically with "Nichrome" ribbon. Then it was passed through a train of Emmerling towers, containing in turn beads drenched with silver nitrate solution, solid potassium hydroxide which had been fused with a small proportion of permanganate, and beads drenched with concentrated sulphuric acid to which a trace of potassium dichromate had been added. Finally the air was dried in a long tube containing phosphorous pentoxide which had been resublimed in air. The apparatus was constructed wholly of glass with fused or ground joints throughout. The joints were either dry or lubricated with sulphuric acid, except in the case of a two-way stop cock beyond the phosphorous pentoxide tube, which was lubricated with Ramsay grease. Since ferric oxide quickly came to constant weight when ignited in this air, it was obviously sufficiently pure for the purpose.

Oxygen. Oxygen prepared by the Linde Air Products Company was purified in the same apparatus as that used for purifying air. This gas contained about 97 per cent. of oxygen. Apparently a large percentage of the impurity was argon.[1]

Hydrogen. At first, because of convenience, hydrogen was generated by the action of water on " Hydrone ". It was scrubbed with water in a tower filled with moist glass wool and was then dried with fused potassium hydroxide and finally phosphorous pentoxide. This gas proved to be unsatisfactory, for when it was passed through a hot quartz tube for some time, a black deposit which appeared to be carbon was formed and iron reduced from the oxide in this gas showed a continuous gain in weight owing apparently to absorption of carbon. Since it seemed probable that this hydrogen contained hydrocarbons, an electrolytic method of generating the gas was substituted. The generator contained the system zinc amalgam-dilute hydrochloric acid-platinized platinum, and has already been shown to give very pure hydrogen.[2] Two such generators yield a current of hydrogen sufficiently rapid for most purposes and by applying an external electromotive force, the evolution of gas can be made much more rapid. After purification by scrubbing with dilute potassium hydroxide solution and drying by freshly fused potassium hydroxide and resublimed phosphorous pentoxide, this hydrogen gave no evidence of impurity of any sort. For some time after the charging of the generators with fresh acid, the gas undoubtedly contains air originally dissolved in the acid, but in the course of time this must be gradually swept out by the continuous flow of minute bubbles of hydrogen. The apparatus was constructed entirely of glass, with ground stoppers, except for two very short rubber connections which were used to join the generators to the purifying train. The ground joints were lubricated with Ramsay grease.

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[1] Morey, Jour. Amer. Chem. Soc., **34**, 491 (1912).

[2] Cooke and Richards, Proc. Amer. Acad., **23**, 149 (1887).

PURIFICATION OF FERRIC OXIDE

Two specimens of ferric nitrate were purified for conversion into ferric oxide. Sample A was of terrestrial, Sample B of meteoric origin.

Sample A was prepared from the same specimen of pure iron, manufactured by the American Rolling Mills Co., that was used in the previous investigation upon ferrous bromide. This material contains sulphur 0.019 per cent., phosphorous, 0.003 per cent., carbon 0.018 per cent, copper 0.05 per cent., and traces of silicon and manganese, less than one-tenth of one per cent. in all. A block of this iron was washed with ether, alcohol and water, and was etched with pure nitric acid to remove surface contamination. It was then placed in a large platinum dish and treated with several successive portions of fifty per cent. nitric acid, until about one hundred grams were dissolved. In order to remove a small amount of insoluble material, chiefly carbon and basic nitrate, the solution, which still contained a large excess of nitric acid, was filtered by suction through a carefully prepared asbestos mat in a platinum funnel into a quartz flask. Next the solution was transferred to a large platinum dish and evaporated to crystallization, on an electric stove in order to avoid introduction of sulphur compounds from a gas flame. The crystals were freed as far as possible from mother liquor by centrifugal drainage in an apparatus in which the material could come in contact only with platinum,[1] and were rinsed in the centrifuge with concentrated nitric acid. The crystals were then recrystallized four times from concentrated nitric acid, with all the foregoing precautions. The mother liquor of the first crystallization was evaporated until a second crop of crystals could be obtained and this second crop was recrystallized three times from the successive mother liquors of the first set of crystals. The two final crops of crystals were converted separately into a mixture of oxide and basic nitrate by heating them in small portions in a platinum dish on an electric stove. The best material is designated Sample A_1, that recovered from the mother liquors Sample A_2.

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[1] Baxter, Jour. Amer. Chem. Soc., **30**, 286 (1908).

In order to show that mere crystallization of the nitrate is sufficient to eliminate the predominating metallic impurities, about one hundred grams of ferric nitrate were rendered impure with one gram each of copper, nickel, aluminum, and manganese nitrates and the mixture was recrystallized. After two crystallizations the crystals were found free from copper, nickel and manganese by tests with ammonia, dimethylglyoxime, and alkaline fusion respectively, and, while the second crop of crystals contained a trace of aluminum, the third crop gave no indication of the latter element when treated with an excess of sodium hydroxide and the filtrate tested with ammonium chloride.

The purification of the meteoric material, owing to the larger proportion of impurity was necessarily more difficult and prolonged. A new portion (80 grams) of the " Cumpas " meteorite, found near Cumpas, Senora, Mexico, in 1903, was very kindly given to us by Professor John Eliot Wolff, Curator of the Harvard Mineralogical Museum. This meteorite, which was used in the investigation by Baxter and Thorvaldson,[1] contains about 88 per cent. of iron, the remainder being chiefly nickel. Although the method used by Baxter and Thorvaldson for the elimination of the nickel was a tedious one, yet comparison on a small scale with other methods failed to show any marked advantage of any one of the latter, so that the process used in the earlier work was adhered to.

After the metal had been cleaned with ether and alcohol and etched with nitric acid, it was dissolved in redistilled hydrochloric acid, and an insoluble residue, consisting largely of graphite, was removed by filtration. The solution was next diluted considerably and saturated with hydrogen sulphide which had been thoroughly scrubbed with water. The precipitate produced in this way, chiefly sulphur, was removed, and after nearly neutralizing the free acid with ammonia, the solution was again saturated with hydrogen sulphide. The black precipitate, which contained little but ferrous sulphide, was discarded. A large excess of ammonia was then added and hydrogen sulphide in excess passed in. The precipitated sulphides were washed several times with water containing ammonium chloride made from distilled reagents, and were transferred to a large washed filter where they were extracted with two per cent. hydrochloric acid. Since the solution still contained considerable nickel after two repetitions of this process, the remainder of the nickel was eliminated by precipitating the iron as ferric hydroxide. The solution of ferrous chloride was oxidized with nitric acid and after dilution to nearly ten liters was poured into a large excess of redistilled ammonia in equal volume. The precipitate was washed by decantation three times and was dissolved in redistilled nitric acid. This process was repeated six times before nickel could not be detected by means of ammonium sulphide in the mother liquor after concentration in small volume. Even in the seventh filtrate dimethylglyoxime showed traces of nickel to be present, but these traces were undoubtedly eliminated in the subsequent processes.

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[1] Loc. cit.

The seventh precipitate of ferric hydroxide was dissolved in an excess of redistilled sulphuric acid with the assistance of a small amount of nitric acid, and the sulphate was freed from nitric acid by evaporation and heating. The ferric sulphate was next electrolytically reduced to ferrous sulphate in a large platinum dish which served as cathode, while a spiral of heavy platinum wire formed the anode. The solution was originally so concentrated and the solubility of the ferrous sulphate was so much reduced by the sulphuric acid originally present together with that formed in the reduction, that, on cooling the solution after the passage of a heavy current for some time, ferrous sulphate crystallized out. Electrolysis with intermittent cooling and evaporation was continued until the greater portion of the iron was obtained in the form of ferrous sulphate. This ferrous sulphate was once recrystallized from aqueous solution with centrifugal drainage. Iron was next deposited in the metallic state by electrolysis in ammonium oxalate solution. A warm concentrated ammonium oxalate solution was nearly saturated with ferrous oxalate by adding ferrous sulphate solution and the solution was electrolyzed hot with a high current density in a large platinum dish which served as cathode. From time to time recrystallized oxalic acid was added in order partially to provide for loss at the anode. Occasionally the metallic deposit was thoroughly washed with water and dissolved in redistilled nitric acid. During the electrolysis there was absolutely no evidence of the deposition of manganese dioxide on the anode. When all the material had been thus electrolyzed, the accumulated solution of ferric nitrate was filtered, evaporated and crystallized six times exactly in the manner previously described. The nitrate in turn was ignited to oxide and basic nitrate. Since crystallization of the nitrate alone would probably have sufficed to eliminate the impurities, there can be little doubt in light of the protracted series of operations to which the meteoric material was subjected, that the final product was sufficiently freed from known impurities.

PREPARATION OF THE FERRIC OXIDE FOR WEIGHING

The ignition of the ferric oxide in air and its subsequent reduction in hydrogen were carried on in a quartz tube which formed part of a bottling apparatus[1] by means of which the platinum boat containing the material could be transferred to a weighing bottle in a current of dry gas without the slightest exposure to moisture. The tube was electrically heated by a removable mica sleeve wound with " Nichrome " resistance ribbon, while the control of temperature was secured through external resistance. By this method a temperature of 1200° can readily be secured. But at that temperature the life of the coil is precarious, and furthermore not only was the outside of the quartz tube attacked where it came in contact with the mica, but the platinum boat showed signs of adhering to the quartz. Hence in actual practice the temperature was not allowed to exceed about 1100°. That the temperature was actually as high as this was shown by the fact that silver melted readily at temperatures below the maximum employed. Even under these conditions the outside of the quartz tube suffered where it came in contact with the mica so that occasionally its surface was renewed by firepolishing in an oxyhydrogen flame.

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[1] Richards and Parker, Proc. Amer. Acad., **32**, 59 (1896); Zeit. anorg. Chem., **13**, 85.

Since, if ferric oxide is reduced in contact with platinum, the metals alloy to so considerable an extent that it is a very difficult matter subsequently to remove the iron, the boat was entirely lined with thin platinum foil. Although of course the iron alloyed with the lining of the boat, this lining was replaced with one of new platinum foil in each determination. In this way the boat was entirely prevented from attack in all but a few cases where a small amount of oxide accidentally found its way between the boat and lining and occasioned some difficulty.

The boat was prepared for analysis by scouring with sea sand, igniting in a blast flame, and boiling with hydrochloric acid, the operations being repeated several times. Next the lining was constructed of new platinum foil and boiled with hydrochloric acid several times more. Then the boat was ignited in the quartz tube for several hours in a current of pure dry air and after it had been allowed to cool was transferred by means of the bottling apparatus to the weighing bottle in which it was eventually weighed by comparison with a similar counterpoise.

Owing to accidental contamination of the boat with iron in one of the earlier experiments, in the next analysis, after thorough cleansing, the boat and lining were weighed after ignition both in air and in hydrogen. A loss of 0.2 milligram was found after the ignition in hydrogen. In subsequent experiments with the same boat the difference in weight after ignition in air and in hydrogen gradually diminished to about 0.1 milligram but never entirely disappeared. Reversing the order of the ignition failed to change the nature of magnitude of the difference. In one of the later analyses a comparatively new boat, which had never been contaminated with iron, was tested in a similar way with an exactly similar result. While the cause of the difficulty was not further investigated, a probable explanation of the difference in weight is the presence of a trace of iron or a similar metal in the material of the boat or lining. In any case error could obviously be avoided by determining the difference in the weight of the boat when ignited in air and in hydrogen, and allowing for this difference in computing the weights of the ferric oxide and the metallic iron. This method of correction was actually followed.

After the boat with its lining had been treated as above and weighed, it was filled with the mixture of oxide and basic nitrate, which had been powdered in an agate mortar, and it was heated in the quartz tube in a current of pure dry air, gently at first until decomposition of the nitrate was essentially complete, finally at about 1000° for several hours. After the boat had cooled, it was transferred to the weighing bottle by means of the bottling apparatus and weighed. The heating in air was then continued until the weight of the boat and contents became constant within a few hundredths of a milligram. Usually ten to fifteen hours was a sufficiently long period to produce this result, although for sake of convenience the heating was frequently prolonged over night.

Although the very fact that the weight of the oxide becomes constant when it is treated in this way is evidence that the ferric oxide does not appreciably dissociate into a lower oxide and oxygen even at the highest temperatures employed, experiments were undertaken to test this point early in the investigation. One specimen of oxide was several times ignited in a current of oxygen, and, after it had cooled, it was bottled in dry air. As soon as the weight was constant, the material was ignited and cooled in air in the usual way. A loss in weight of 0.2 milligrams in 5 grams of oxide was found. Re-ignition in oxygen yielded the original weight and upon second ignition in air the weight became practically the same as after the first ignition in air.

The higher weight of the oxide after ignition in oxygen was confirmed in a second similar series of experiments. Furthermore it was found that the boat and lining when treated similarly showed no perceptible difference in weight under the different conditions.

It seemed hardly probable that the difference was due to dissociation of the ferric oxide, however, but rather to occlusion of either oxygen or higher oxide by the ferric oxide. This view was substantiated by experiments in which ferric oxide was heated in nitrogen and in a vacuum. Nitrogen, free from both oxygen and hydrogen, was prepared in an all glass apparatus kindly loaned by Dr. C. J. Moore.[1] Ferric oxide, which had been ignited to constant weight in air, was heated for four hours in nitrogen and cooled in this gas before being bottled in air. As a result of this treatment 7.5 grams of oxide lost 0.6 milligram. In order to prove conclusively that this loss was due to dissociation of the ferric oxide into a lower oxide and oxygen, owing to a low oxygen pressure, another sample of oxide was heated in the bottling apparatus which was kept as completely exhausted as possible by means of an efficient Töpler pump. During this treatment a small amount of gas was evolved continually and a loss in weight of 1 milligram was observed. Both of the latter experiments lead to the conclusion that the dissociation pressure of the oxygen from ferric oxide is at any rate very low at the highest temperatures employed in this work and therefore that no loss of oxygen could have taken place from this cause when the oxide was heated in air.

The results of the investigations of others support this view. Walden[2] found by heating ferric oxide in a vacuum no measurable pressure of oxygen below 1050°C. and at 1100° the observed pressure was only 5mm. Hilpert[3] found by chemical tests that the velocity of dissociation is very small.

The safest course to pursue seems to be to assume the weight of the oxide after ignition to constant weight in air to be correct, although it is worth pointing out that if the weight after ignition in oxygen is used, the results of this research will be lowered by about seven one-thousandths of a unit.

Attention has been called by Richards[4] to the fact that most oxides made by the ignition of nitrates retain small amounts of nitrogen and oxygen, but Richards and Baxter[5], in the earlier research upon ferric oxide showed that ferric oxide is an exception to this rule, in that the quantity of occluded gases is negligible for the purpose in hand.

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[1] Baxter, Moore and Boylston, Proc. Amer. Acad., **47**, 588 (1912); Jour. Amer. Chem. Soc., **34**, 261 (1912); Zeit. anorg. Chem., **74**, 365.

[2] Jour. Amer. Chem. Soc., **30**, 1350 (1908).

[3] Ber. d.d.chem. Ges., **42**, 4893 (1909).

[4] Proc. Amer. Acad., **26**, 281 (1891); **28**, 200.

[5] Proc. Amer. Acad., **35**, 257 (1900); Zeit. anorg. Chem., 23, 250.

THE REDUCTION OF FERRIC OXIDE

In order to reduce the ferric oxide, the boat and bottle were placed in their proper places in the bottling apparatus and, when the air had been nearly displaced by pure hydrogen, the boat was gradually heated until the reduction progressed rapidly. Owing to the fact that the reaction is an exothermic one, it was usually necessary to retard the reduction by removing the heating coil after the reduction had commenced. As soon as this portion of the process was past, heating was resumed and continued at dull redness as long as perceptible amounts of water were evolved. Since the reduced metal sinters to a considerable extent even at a relatively low temperature, it seemed better to avoid this effect as far as possible until reduction was essentially complete. The temperature was then very gradually increased to a bright red heat, and finally was maintained at 1050-1100° for several hours. The boat was next cooled in hydrogen, the hydrogen was displaced by air and the boat was bottled and weighed as in the case of the oxide. The metal was then heated again for several hours at bright redness and again cooled and weighed, and the process was repeated until the weight became constant within a few hundredths of a milligram. In the earlier analyses four or five ignitions were found necessary to secure constant weight. Eventually time and labor were saved by prolonging the first heating in hydrogen to 60 hours or more. When this was done, no change in weight of more than 0.1 milligram was ever observed after the first heating, even when the second heating was as long as 50 hours. This constancy in the weight of the metal indicates not only that reduction had proceeded as far as it would go under the conditions of the experiment, but also that neither the platinum nor the iron volatilized appreciably even at the highest temperature employed.

While it is a well-known fact that very finely divided iron is pyrophoric, we were able to secure evidence of only very slow oxidation of the highly sintered and compact metal which resulted from the reduction. The appearance of the metal did not alter on long standing even in an atmosphere of average humidity. Furthermore on standing eighteen hours in the weighing bottle in a dessicator, in five experiments the observed gain in weight was only 0.12, 0.03, 0.01, 0.04 and 0.05 milligram respectively. In the light of these facts it seems reasonably certain that in dry air iron oxidizes so slowly that at any rate no error was introduced from this source before the metal was weighed.

After six analyses had been completed, it was noticed in the next experiment, while the nitrogen was being displaced by air, that a slight mist appeared on the tube beyond the boat and that the portion of the tube containing the boat became perceptibly warmer than the adjacent portions. In a short time the water evaporated into the current of dry air, leaving the iron unchanged in appearance. This phenomenon was not observed in the earlier experiments, because in these the boat was concealed by the heating coil which had been allowed to cool *in situ.* In a later experiment when the empty boat was treated in the same way a similar occurrence took place, so that the first conclusion that the union of the hydrogen and oxygen was catalyzed by the finely divided iron is by no means certain. Although no attempt was made to settle the latter point, experiments were immediately undertaken to determine whether perceptible oxidation of the iron was brought about during the formation of the moisture or by its presence. This was done by first weighing the reduced iron after displacing the hydrogen with air. Then the metal was again ignited and cooled in hydrogen, but before the air was admitted to the bottling apparatus, this was exhausted as completely as possible by means of a Töpler pump. The iron did not lose perceptibly in weight during this treatment and a repetition of the experiment yielded the same result. While it is evident that the earlier experiments had fortunately not been vitiated by this newly discovered occurrence, in all the subsequent analyses the precaution was taken to exhaust the bottling apparatus, after the iron had been allowed to cool in hydrogen, before admitting the air. The result of these experiments is entirely in accord with the experience of Friend, Hull and Brown[1] and of Friend;[2] for the former have shown that steam affects iron only slightly at 500° while the latter proved that steam has no effect at 200-300°.

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[1] Jour. Chem. Soc., 99, 969 (1911).

[2] Jour. Iron and Steel Inst., ii, 172.

Although Baxter[1] has already investigated the occlusion of hydrogen by finely divided iron which has been heated and cooled in an atmosphere of the gas, and found no positive evidence of occlusion, the subject was further investigated in several of the analyses of this research. The boatload of iron which had been brought to constant weight when cooled in an atmosphere of hydrogen, was again ignited in hydrogen, and while it was still red hot, the bottling apparatus was rapidly exhausted so that the metal cooled in a vacuum. Then air was admitted and the boat was bottled and weighed. No change in weight beyond the error of weighing could be detected, and a repetition of the experiment yielded the same result. Even though it was thus proved to be safe to allow the metal to cool in hydrogen, in many of the later experiments the final weight of the metal was obtained after cooling in a vacuum.

Sieverts[2] found that iron at 800° dissolves per 100 grams only 0.2 milligram hydrogen and that the amount dissolved diminishes with decreasing temperature.

From the above experiments it is obvious also that the platinum of the boat and lining could have occluded no appreciable amount of hydrogen. Furthermore, Sieverts and Jurisch[3] found that platinum heated and cooled in hydrogen retained no measurable amount of the gas.

In the earlier paper upon the analysis of ferric oxide, the effect of the earth's magnetism upon the weight of the iron was shown both theoretically and experimentally to be insignificant.

The following tables include the results of all the analyses which were undertaken, with the exception of one preliminary analysis in which impure hydrogen made from hydrone was employed.

The weighings were made entirely upon a No. 10 Troemner balance sensitive to 0.02 milligram, which is used only for the most exact work. The weighing bottle was always compared by substitution with a counterpoise of the same weight and shape containing a mass of platinum equal to that of the boat. The weights were standardized to hundredths of a milligram by the method proposed by Richards.[1] Ample time was always allowed the boat and counterpoise to come to equilibrium with the atmosphere of the balance case.

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[1] Amer. Chem. Jour., **22**, 363 (1899).

[2] Zeit. Electrochem., **16**, 707 (1910).

[3] Ber. d.d.chem. Gesell., **45**, 221 (1912).

A vacuum correction of +0.000086 gram was added for every apparent gram of ferric oxide and of +0.000008 for every apparent gram of metal, the densities of these substances and the weights being assumed to be 5.2, 7.9 and 8.3 respectively.

In the first two analyses the weight of the empty boat after ignition in hydrogen was not determined. Since, however, a new boat with its lining was found to lose in weight by 0.1 milligram when ignited in hydrogen after ignition in air, a correction of this amount is applied in Analyses 1 and 2. In the first five analyses after the reduction of the oxide to metal the hydrogen was displaced by a current of air, but in all others the bottling apparatus was freed from hydrogen by exhaustion before air was admitted.

SERIES I. $O = 16.000$

Number of analysis	Sample of Fe_2O_3	Weight of Fe_2O_3 in vacuum	Weight of Fe in vacuum	Ratio $Fe_2:Fe_2O_3$	Atomic Weight of Iron
		Grams	Grams		
1	A_1	4.86111	3.39995	0.699418	55.845
2	A_1	7.59712	5.31364	0.699428	55.847
3	A_1	6.50945	4.55298	0.699442	55.851
4	A_1	8.00040	5.59576	0.699435	55.849
5	A_1	7.27260	5.08661	0.699421	55.846
6	A_2	7.69441	5.38155	0.699410	55.843
7	A_2	7.33754	5.13213	0.699435	55.849
		Average		0.699427	55.847

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[1] Jour. Amer. Chem. Soc., 22, 144 (1900).

SERIES II. O = 16.000

Number of analysis	Sample of Fe_2O_3	Weight of Fe_2O_3 in vacuum	Weight of Fe in vacuum	Ratio $Fe_2:Fe_2O_3$	Atomic Weight of Iron
		Grams	Grams		
8	M	4.46431	3.12240	0.699414	55.844
9	M	4.85179	3.39351	0.699435	55.849
10	M	5.21397	3.64674	0.699417	55.845
11	M	5.99087	4.19030	0.699448	55.853
12	M	6.70197	4.68752	0.699425	55.847
Average				0.699428	55.848
Average of all 12 analyses				0.699427	55.847

An examination of these results shows very satisfactory agreement, not only between the results in each series, but also between the averages of the two series. The highest value found for the atomic weight of iron in either series is 55.853, and the lowest 55.843. The difference, 0.010, corresponds to a variation in the weight of iron obtained from 5 grams of oxide of only about 0.0002 gram.

It is obvious that terrestrial and meteoric iron are identical so far as this examination is capable of testing the point. No other outcome was to be expected, however, especially in the light of the previous comparison of the two sorts of material by Baxter and Thorvaldson.[1]

The average of all twelve analyses, 55.847, is lower than that previously obtained by the reduction of ferric oxide, 55.883, by 0.036 unit. This difference is undoubtedly due to more complete reduction, owing to the higher temperature secured, although the longer periods of continuous ignition in hydrogen must have produced beneficial effects in the same direction.

On the other hand the average result is almost exactly 0.01 unit higher than that found by Baxter, Thorvaldson and Cobb[2] and by Baxter and Thorvaldson[1] through the analysis of ferrous bromide 55.838 (Ag = 107.880). It is hardly probable that the difference between the results of the analyses of ferrous bromide and ferric oxide is due to an incorrect assumption concerning the atomic weight of silver in the calculation of the bromide analyses, as is shown by the following table containing the results of the latter analyses calculated on the basis of various values for silver.

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[1] Loc. cit.

[2] Loc. cit.

If Ag =	Fe =
107.910	55.854
107.900	55.848
107.890	55.843
107.880	55.838
107.870	55.833

In order to produce agreement beteeen the bromide and oxide series of analyses, it would be necessary to assume the unreasonably high value for the atomic weight of silver of 107.90.

If the bromide analysis is assumed to be correct and to yield the value 55.838 (Ag = 107.880), this would indicate incomplete reduction of the ferric oxide, to the extent of 0.0002 gram residual oxygen in the metal resulting from 5 grams of oxide. Such a result would not be at all surprising, however, when the great difficulty in completely converting one solid into another without intermediate fusion or solution is considered.

Whether the atomic weight of silver is taken as 107.880 or 107.870, the averages of the bromide and oxide results, 55.843 and 55.840, when expressed to two decimal places are identical.

The outcome of this research may be briefly expressed as follows:

1. Pure ferric oxide on reduction in hydrogen is found to contain 0.699427 per cent. of iron, whence the atomic weight of iron is 55.847.
2. Terrestrial and meteoric material are found to give identical results.
3. When the result of this investigation is combined with that of the analysis of ferrous bromide by Baxter, Thorvaldson and Cobb, the atomic weight of iron is found to be 55.84.

We are greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in carrying out this investigation.

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[1] Loc. cit.

SUR L'ADSORPTION DES MATIÈRES COLORANTES PAR LES OCRES

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Dans une étude précédente[1] j'ai signalé que les ocres étaient susceptibles d'adsorber les matières colorantes en dissolution et pouvaient, ainsi modifiées, être utilisées industriellement.

Depuis longtemps, on avait cherché à colorer les ocres par simple mélange en les additionnant surtout de couleurs d'aniline, mais la matière colorante incorporée sous cette forme était la plupart du temps entrainée au lavage, elle était peu solide et les nuances ainsi produites d'abord belles et vives s'effaçaient lentement sous l'action de la lumière.

Le résultat est tout-à-fait différent si la matière colorante est fixée sur l'ocre par adsorption; le corps insoluble (ocre) et le corps soluble (matière colorante) s'unissent de manière que le lavage ne peut plus les séparer. La matière colorante, en perdant sa solubilité, a acquis l'adhérence au corps insoluble; mais les deux corps ont gardé leurs propriétés physiques et chimiques. Un nouveau dissolvant peut de nouveau les séparer sans altération. Enfin, les couleurs ainsi obtenues sont solides à la lumière.

J'ai déterminé,[2] pour un certain nombre de matières colorantes, le pouvoir adsorbant d'ocres d'origine et d'état physique (finesse des particules) différents; j'ai trouvé que l'adsorption pour 100 gr. de la même terre et dans les mêmes conditions d'expérience, variait de 4,23 dans le cas de la Safranine G à 0,2 pour le Violet à l'acide ou la Rhodamine B.

Pour compléter ces recherches, j'ai fait entrer en jeu les facteurs qui pouvaient favoriser ou retarder l'adsorption, notamment la température, les acides, les bases, les sels.

Influence de la température. L'élévation de la température accélère l'adsorption et la précipitation des particules d'ocre en suspension; les essais ont été faits suivant les indications déjà données, avec le bleu de nuit, la parafuchsine, le violet cristallisé et le vert malachite.

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[1] Bull. Soc. Chim. (4) t. 11, p. 454, 1912.

[2] Bull. Soc. Chim. (4) t. 11, p. 460, 1912.

J'ai opéré de la façon suivante avec des solutions portées à l'ébullition: On prépare 10 vases à précipiter de 2 litres contenant chacun 20 grammes d'ocre. On verse sur la substance 500 grammes d'eau bouillante, puis on ajoute, en quantité croissante, de la solution colorée (contenant 1 gr. de matière colorante par litre); le premier récipient recevra un volume de liqueur colorante supérieur de 100 cc à la quantité nécessaire pour saturer l'ocre à froid; le second en aura 100 cc de plus que le premier, et ainsi de suite jusqu'au dixième. On laisse reposer 24 heures après avoir agité fréquemment pendant les 3 premières heures et on cherche par comparaison colorimétrique, le récipient contenant la liqueur surnageante la plus voisine du terme de saturation. Soit *n* le nombre de cc de matière colorante contenue dans la solution primitive; on repète la même expérience que précédemment, mais en ajoutant cette fois successivement n+10, n+20, n+90 cc de colorant. On laisse de nouveau déposer pendant 24 heures et on prend, comme ci-dessus, l'ocre ayant adsorbé le maximum de matière colorante (la liqueur surnageante restant incolore).

On obtient une valeur suffisamment approchée du pouvoir adsorbant que l'on rendra encore plus rigoureuse en procédant. Suivant le même principe, à une troisième expérience.

Matières colorantes	Ocre transparente IS, Lefranc et Cie	
	Poids de couleur adsorbée à 100° par 100 gr. d'ocre	Poids de couleur adsorbée à 15° par 100 gr. d'ocre
Bleu de nuit	5,85	3,62
Parafuchsine	2,10	1,92
Violet cristallisé	5,12	4,10
Vert malachite		3,07

Ocres modifiées par la chaleur: Variations du pouvoir adsorbant. J'ai déterminé en outre de quelle façon variait le pouvoir adsorbant quand les ocres avaient été *préalablement* chauffées, puis refroidies.

D'après Suida,[1] les silicates perdent leur pouvoir adsorbant quand on les chauffe au rouge. Pelet et Mazoli[2] ont montré qu'il en est de même de Fe_2O_3 chauffé. Il semblerait logique que les ocres qui sont des argiles à base d'hydrates ferriques, possèdent la même propriété. Or, l'ocre "transparente," firme Lefranc, portée à 700° pendant $\frac{1}{2}$ heure, a un pouvoir adsorbant très voisin de celui de la terre non chauffée: 3,62 pour le bleu de nuit avec l'ocre jaune; 3,58 avec l'ocre rouge. Il faut chauffer les ocres longtemps, et à une température supérieure à 700° pour diminuer la faculté d'adsorption.

Ce résultat est intéressant, car il permet d'augmenter la gamme des nuances; ainsi, l'ocre jaune, à son maximum d'adsorption, donne avec le bleu de nuit la teinte bleu de nuit, tandis que, dans des conditions identiques, la même terre, devenue rouge (par action de la chaleur à 700°) donne une belle nuance noire.

Influence de la concentration des solutions. Les expériences précédentes ont été faites sur des solutions contenant 1 gr. de matière colorante par litre d'eau. Si on opère sur des solutions plus concentrées, on constate que l'adsorption n'est pas directement proportionelle à la concentration: elle est relativement plus grande avec les solutions diluées. La rapport de la quantité de matière colorante adsorbée à la concentration de la solution diminue si la concentration augmente. Le fait est très net avec le bleu de nuit et le violet cristallisé.

D'après Biltz et Steiner,[3] qui ont étudié l'adsorption de bleu de nuit par le noir animal, ce phénomène tiendrait à la nature basique des colorants et à leur hydrolyse en solution aqueuse.

Influence de l'acidité des solutions. Tantôt les acides favorisent l'adsorption, tantôt ils la retardent, tantôt ils n'ont pas d'action; les teintes varient peu. Par contre, la précipitation de la terre en suspension est accélérée.

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[1] Mon. f. Chem. t. 25, p. 1107-1133, 1904.

[2] Bull. Soc. Chim. t. 5, p. 1015, 1909.

[3] Zeit. Chem. Ind. Kolloid. t. 7, p. 113, 1910.

Matières colorantes	Acidité	Ocrs transparente IS, Lefranc et Cie	
		Poids de couleur adsorbée par 100 gr. d'ocre en liqueur acide	Poids de couleur adsorbée par 100 gr. d'ocre en liqueur neutre
Vert malachite	1 gr SO_4H_2 par 1000 cc d'eau	3,75	3,07
Violet cristallisé	do	3,90	4,10
Bleu de nuit	do	3,77	3,62
Safranine G	do	6,10	4,23
Ecarlate double brillant	do	0,82	1,02
Noir diamine B H	do	2,61	1,17

Influence de l'alcalinité des solutions. Les alcalis retardent beaucoup la précipitation de l'ocre en suspension dans la solution; très souvent, ils décomposent la matière colorante, sinon ils retardent l'adsorption et les teintes sont modifiées.

Le tableau comparatif ci-dessous donne les résultats obtenus avec quelques colorants non décomposés par la base.

Matières colorantes	Alcalinité	Ocre transparente IS, Lefranc et Cie	
		Poids de couleur adsorbée par 100 gr. d'ocre en liqueur alcaline	Poids de couleur adsorbé par 100 gr. d'ocre en liqueur neutre
Safranine G	1 p. 1000 KOH	1,92	4,23
Noir diamine BH	do	0,86	1,17
Ecarlate double brillant G	do	0,19	1,02

Influence des sels. La faculté d'adsorption se manifeste aussi en présence des sels, tels que Na Cl, SO_4Na_2. En présence de Na Cl en particulier, le pouvoir adsorbant s'élève et l'adsorption se fait plus rapidement. Selon Pelet-Jolivet et Wild,[1] ce phénomène tiendrait à ce que l'addition d'un électrolyte sur le colorant diminuerait la solubilité du colorant. D'autre part, les matières colorantes possèdent la propriété de passer très facilement, sous l'action d'électrolytes convenables, à l'état colloidal; cette coagulation colloidale a donc une influence marquée sur l'adsorption.

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[1] Bull. Soc. Chim. (4) t. 3, p. 274, 1907; p. 1090, 1908.

Mes essais ont été faits en dissolvant 4 gr. de Na Cl par litre de solution colorante et en procédant comme je l'ai expliqué. On peut ainsi obtenir des ocres très chargées en colorant.

J'ai remarqué que la matière colorante fixée, en présence de Na Cl, paraît avoir une adhérence moins grande que dans les autres cas. C'est ainsi que l'eau bouillante en entraîne une quantité appréciable.

Matières colorantes	Electrolyte	Ocre transparente Lefranc et Cie	
		Poids de couleur ads. p. 100 gr. d'ocre en prés. de NaCl	Poids de couleur ads. p. 100 gr. d'ocre en solution aqueuse
Bleu de méthylène	4 p. 1000 NaCl	6,38	3,80
Violet crist.	do	8,25	4,10
Parafuchsine	do	3,10	1,92

Nature du dissolvant. La quantité de colorant assorbé dépend encore de la nature du dissolvant. C'est que le pouvoir adsorbant est beaucoup plus élevé en solution aqueuse que dans l'eau alcoolisée; l'adsorption cesse complètement pour une teneur trop grande en alcool. On peut même extraire, par l'alcool, le colorant de l'ocre teinte en solution aqueuse.

Dreaper et Davis[1] ont constaté qu'une solution de bleu de nuit, ayant traversé une colonne de sable, est acide au tournesol; Suida,[2] opérant sur l'amidon et les silicates, aurait trouvé dans le bain la totalité de l'acide venant du sel coloré. Dans aucun de mes essais, la solution surnageante n'a d'action sur le tournesol.

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[1] Chem. Indust. t. 31, p. 100, 1912.

[2] Mon. f. Ch. t. 25, p. 1107, 1904.

ON THE EFFECT OF FREE CHLORINE UPON THE PRODUCT OF HYDROLYSIS OF TELLUROUS CHLORIDE

By Philip E. Browning and George O. Oberhelman

New Haven, Conn.

In 1909 Browning and Flint,[1] after an extended hydrolysis of tellurous chloride, obtained two fractions which by three methods gave atomic weights of approximately 126.5 and 128.5. The first value was obtained from the more easily hydrolysable fraction and the second from the less easily. The tellurous chloride used was prepared from purified tellurium which gave an atomic weight of 127.5, the accepted value.

Since the publication of the preliminary paper describing this work, the investigation has been continued by Flint,[2] who in 1910 published an account of a more extended hydrolytic treatment, resulting in a further lowering of the atomic weight in the more easily hydrolyzed fraction.

More recently Harcourt and Baker,[3] starting with a sample of telluric acid of assumed purity and reducing it to tellurous chloride by boiling with hydrochloric acid, made a series of four fractional hydrolyses and found no evidence of the lowering of the atomic weight. In making the determinations of the atomic weight they used a different method from any of the three employed by Browning and Flint. In order to explain Flint's results, they suggest the presence of an impurity in the tellurium used by him, a hypothesis which seems unlikely in view of the fact that the atomic weight of the original material was shown to be 127.5, the accepted value. They also state that no atomic weight determination of the less hydrolysable fraction was made, showing that they had overlooked the value 128.5 given in the first paper, and considered by the authors one of the best evidences of complexity. In continuing their discussion of the reasons for Flint's results, Harcourt and Baker state that the yellow color sometimes observed in the hydrolytic fractions was found by them to be due to a small amount of telluric oxide present in their material presumably because of chlorine set free from the hydrochloric acid by the action of bright sunlight. To investigate the influence of this factor upon Flint's results they took pure telluric oxide and by treating it with nitric acid and drying at 140°, as in making the basic nitrate from tellurous oxide, they obtained a product which on ignition gave a loss of 17.35% of oxygen as against 16.49% given off when pure $2\ TeO_2.\ HNO_3$ is ignited. This seemed to show the formation of a basic nitrate of a higher degree of oxidation; and they stated that if such a salt were present, while the presence merely of $2\ TeO_2.\ HNO_3$ was assumed, the atomic weight determination would result in a value of 118.3 for tellurium.

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[1] Am. Jour. Sci. XXVIII, 347.

[2] Am. Jour. Sci. XXX, 209.

[3] Trans. Chem. Soc. (London) XCIX, 1311.

In order to investigate the conclusions of Harcourt and Baker with regard to the effect of free chlorine upon the product of the hydrolysis of tellurous chloride the following experiments have recently been made.

EXPERIMENT I—About 150cm.^{3} of pure hydrochloric acid was placed in a glass stoppered bottle of 250cm^3 capacity and allowed to stand in the bright sunlight for three days. A portion of this acid, 20cm.^{3}, was then placed in a distillation apparatus frequently used in iodometric processes and consisting of a Voit flask, serving as a retort, sealed to the inlet tube of a Drexel wash bottle, the outlet tube of which was trapped by sealing on Will and Varrentrapp absorption bulbs. A solution of potassium iodide was placed in the Drexel wash bottle and also in the absorption bulbs, and the wash bottle was kept immersed in cool water. Before beginning the distillation a current of carbon dioxide was passed through the apparatus to expel the air, and after the distillation the gas was again passed until the apparatus was cool. The 20cm.^{3} of the hydrochloric acid which had been exposed to sunlight was boiled in this apparatus to a volume of 10cm.^{3} and the amount of chlorine liberated was estimated by determining the iodine liberated from the potassium iodide which was determined by the use of a standard thiosulphate solution. By this treatment the 20cm.^{3} of hydrochloric acid set free 0.0038 grm. of iodine which would be equivalent to about 0.0010 grm. of chlorine. Pure hydrochloric acid set free no iodine when subjected to this distillation process. Five grams of pure tellurous oxide were dissolved in 10cm.^{3} of the hydrochloric acid containing chlorine and the solution was poured into 500cm.^{3} of boiling distilled water. Hydrolysis took place at once; and on standing over night the precipitated product was of a pale yellow color. After being filtered, washed and dried, 1 grm. of this precipitate was dissolved, out of contact with the air, in 20cm.^{3} of pure hydrochloric acid contained in the distillation flask above described, and the solution was boiled to 10cm.^{3}. No iodine was liberated from the potassium iodine.

EXPERIMENT II—Five grams of pure tellurous oxide were dissolved in 10cm.^{3} of pure hydrochloric acid and the solution was saturated with chlorine gas. It was then poured into 500cm.^{3} of hot water as in the previous experiment and 1 grm. of the dried faintly yellow product of hydrolysis was treated as in Experiment I. The amount of iodine liberated was 0.0006 grm. equivaent to 0.0004 grm. of telluric oxide.

EXPERIMENT III—Five grams of pure tellurous oxide were dissolved in 10cm.^{3} pure hydrochloric acid, the solution was saturated with chlorine gas, as in the previous experiment, and poured into 500cm.^{3} of hot water. A current of chlorine gas was then passed into the liquid for a half hour. The product which separated was pale yellow, and 1 grm., subjected to the distillation process previously described, yielded 0.0032 grms. of iodine, equivalent to about 0.0022 grm. of telluric oxide.

EXPERIMENT IV—In this experiment the same procedure was followed as in the previous experiment, except that the procedure preparatory to the distillation was repeated twice. A slight deepening of the yellow color was noticed after each treatment. Three closely agreeing results obtained by means of the distillation process gave 0.0062 grm. of iodine for 1 grm. of substance, which is equivalent to 0.0042 grm. of tellurium trioxide, or less than one-half of 1%.

The filtrates from the hydrolyzed products in Experiments II and III were treated with ammonium hydroxide and faintly acidified with acetic acid, in order to precipitate the less hydrolysable tellurous material. After the removal of these small precipitates, the filtrates were evaporated to dryness and 1 grm. each of the residues was dissolved in hydrochloric acid and submitted to the distillation process yielding, respectively 0.0012 grm. and 0.0320 grm. of iodine, and showing amounts of telluric oxide present equivalent to 0.0008 grm. and 0.024 grm., small amounts but larger than in the hydrolyzed products.

It would appear from these experiments that only slight oxidation results when chlorine is present with the hydrochloric acid; and that the amount of telluric oxide carried down with the tellurous oxide in the hydrolysis of tellurous chloride is extremely small, the greater part of the telluric compound remaining in solution, as would be expected. If the yellow color is due to the presence of telluric oxide and not some crystalline or hydrous form of the tellurous compound, that oxide would appear to give coloration quite out of proportion to the amount present.

If pure telluric oxide, on being converted to a basic nitrate, gives a result on ignition of less than ten units on the atomic weight of tellurium, the presence of less than one-half of 1%, obtained by saturating the hydrochloric acid solution with chlorine before hydrolysis would hardly account for the presence of enough basis nitrate in the higher condition of oxidation to have an appreciable effect upon the atomic weight.

SUR LES DERIVES ORGANO-METALLIQUES DE L'ANTIMOINE

PAR MONSIEUR P. CARRE

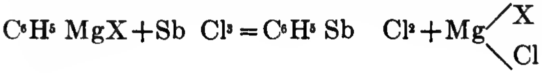
Paris, France

Le présent mémoire a pour but de compléter quelques points relatifs à la triphénystibine et aux chlorures de la mono- et de la diphénylstibine.

La *triphénylstibine* $(C_6H_5)_3Sb$ fut d'abord obtenue par Michaelis et Reese (*Lieb. Ann. chem.*, t. *233*, p. 43) en condensant le chloroure de phényle avec le trichlorure d'antimoine, en solution benzénique, au moyen du sodium. Le rendement obtenu par cette méthode est très faible, il se forme surtout de l'antimoine métallique. Ainsi que l'ont montré Pfeiffer, Heller et Pietzsch (*D. chem. G., t. 37*, p. 4620, 1904) ce composé se prépare beaucoup plus facilement par l'action d'une quantité suffisante de bromure de phényle-mangésium sur le trichlorure d'antimoine.

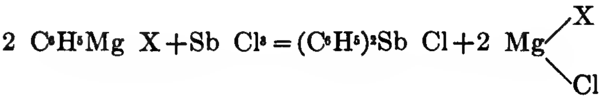
Le *chlorure de la monophénylstibine* $C_6H_5SbCl_2$, se forme, d'après Hasenbaumer (*D. chem. G. t. 31*, p. 2911, 1898) lorsqu'on chauffe la triphénylstibine avec le trichlorure d'antimoine. Selon, Michaelis et Gunther (*D G chem. G., t. 44*, p. 2316, 1911) cette réaction donnerait naissance au *chlorure de la diphénylstibine* $(C_6H_5)_2Sb\,Cl$.

J'ai pensé que ces deux derniers composés s'obtiendraient plus facilement par l'action de 1 ou 2 molécules d'organo-magnésien sur le trichlorure d'antimoine; on conçoit en effet que la réaction puisse se passer conformément aux équations:



$$C^6H^5\,MgX + Sb\,Cl^3 = C^6H^5\,Sb\,Cl^2 + Mg\begin{array}{l}\diagup X\\ \diagdown Cl\end{array}$$

Et



$$2\ C^6H^5Mg\,X + Sb\,Cl^3 = (C^6H^5)^2Sb\,Cl + 2\ Mg\begin{array}{l}\diagup X\\ \diagdown Cl\end{array}$$

Mais, lorsqu'on ajoute avec précaution une molécule d'organomagnésien à la solution éthérée du trichlorure d'antimoine, il se forme surtout de la triphénylstibine et très peu de mono- et de diphénylstibine.

On ne peut du reste obtenir directement les chlorures, car le chlorure de phényle ne forme pas de dérivé magnésien. Il faut s'adresser à l'action du bromure de phényle-magnésium sur le trichlorure d'antimoine, ce qui fournit un mélange de chlorures et de bromures de la mono- et de la diphénylstibine toujours accompagnées d'une forte proportion de triphénylstibine. Pour transformer ce mélange en chlorures et séparer en même temps la triphénylstibine on le traite par une solution de carbonate de soude, ce qui donne les oxydes correspondants C_6H_5SbO et $[(C_6H_5)Sb]_2O$. On lave ces oxydes à l'éther qui enlève la triphénylstibine. La partie insoluble est traitée, à froid, par l'acide chlorhydrique dilué de 2 fois son volume d'eau, ce qui régénère les chlorures C_6H_5SbCl et $(C_6H_5)_2SbCl$.

Lorsqu'on essaye de séparer ce mélange par distillation fractionnée dans le vide, on n'observe pas de point d'ébullition fixe (Michaelis et Gunther indiquent pour le chlorure de la diphénylstibine, 185-230° sous 15 mm.) Cela tient à la facile décomposition par la chaleur de ces chlorures en triphénylstibine et trichlorure d'antimoine suivant les équations:

$$3\ C^6H^5SbCl^2 = (C^6H^5)^3Sb + 2\ SbCl^3$$

$$3\ (C^6H^5)^2SbCl = 2\ (C^6H^5)^3Sb + SbCl^3$$

Le liquide distillé renferme, en effet une assez forte proportion de trichlorure d'antimoine, ainsi que le montre l'action de l'eau qui précipite ce l'oxychlorure d'antimoine alors que le mélange primitif n'est pas décomposé par l'eau.

Cette tendance à la formation de triphénylstibine se manifest déjà à la température ordinaire, au contact de l'acide chlorhydrique, qui enlève peu à peu du chlorure d'antimoine au mélange des chlorures de la mono- et de la diphénylstibine; on constate en même temps que ce dernier s'appauvrit en chlore et que sa composition se rapproche de $(C_6H_5)_2SbCl$, après quelques mois de contact.

C'est sans doute de cette facile décomposition des chlorures de la mono- et de la diphénylstibine que proviennent les divergences des résultats de Hasenbaumer avec ceux de Michaelis.

En *Résumé,* l'action du bromure de phényle-magnésium sur le trichlorure d'antimoine constitue le meilleur mode de préparation des phénylstibines. Cette réaction fournit surtout, même avec une faible proportion d'organo-magnésien, de la triphénylstibine; lorsqu'on emploie une ou deux molécules d'organo-magnésien pour une molécule de trichlorure d'antimoine, il se forme, en même temps que la triphénylstibine, les chlorures de la mono- et de la diphénystibine $C_6H_5Sb\ Cl_2$ et $(C_6H_6)_2Sb\ Cl$. Ces derniers sont décomposés par la chaleur en triphénylstibine et trichlorure d'antimoine.

ACTION OF SOME FLUORINE COMPOUNDS ON CLAY, WATER, ETC.

By D. H. Childs

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Introduction

During the investigation of possibility of making Alumina commercially by heating a mixture of clay and the fluoride of aluminum a large amount of original work was necessary as little is published along that line. Some of the results are set forth in the following:

Questions Involved

To secure as full a discussion as possible, we may look for a moment at the following points of interest, whether they have all been investigated or not.

I. Formation of Hydrofluoric Acid gas from Aluminium Fluroide and steam.
    A. Effect of temperature.
    B. Effect of excess moisture.
    C. Size of grain.
    D. Effect of an added clay.
    E. Character of residue produced, (dusty or not).

II. Effect of Hydrofluoric Acid gas on Clay.
    A. Elimination of Silicia.
        a. Effect of temperature upon rate of elimination.
        b. Effect of size of grain upon rate and completeness.
        c. Effect of excess of steam and concentration of HF.
    B. Elimination of Iron, Titanium, Alkalis, etc.
    C. Formation of aluminium fluoride in the clay.
        a. Effect of temperature.
        b. Effect of steam.

- III. Absorption of Hydrofluoric Acid gas.
  - A. Effect of concentration of the gas.
  - B. Effect of rate of water supply.
  - C. Effect of kind of material in the tower.
    - a. Clay vs. coke.
    - b. Kinds of clay.
    - c. Raw clay or burnt.
    - d. Clay wash on coke.
  - D. Temperature of absorption water.
  - E. State of fluorine after absorption, (HF? H_2SiF_6, or Al_2F_6).
  - F. Effect of length of clay column.
  - G. Effect of excess steam.
- IV. Absorption of Silicon Fluoride.
  - A to G as before, and in addition the following:
  - H. Separation of fluorine from precipitated silica.
  - I. Clogging of pipes by precipitated silica.
- V. Neutralization of acid solutions by clay.
  - A. Effect of kind of clay.
  - B. Effect of temperature at which clay is dried.
  - C. Effect of fineness of clay.
  - D. Temperature of solution. (Effect of)
  - E. Effect of concentration of solution.
  - F. Effect of valence of iron.
  - G. Effect of excess of clay.
    (The effectiveness and value are to be judged by the completeness with which the silica, iron, and titanium are removed from the solution).
- VI. Crystallization and drying of Aluminium Fluoride.
  - A. Evaporation of water, and with it HF (by hydrolysis)
  - B. Solubility of the fluoride.
  - C. Mechanical separation of water from crystals.
  - D. Drying by heat (loss of HF)

VII. Losses.
  A. Fluorine.
    a. In dust from calciner where mix is heated.
    b. In finished oxide.
    c. In gas from absorption tower, as HF or SiF_4
    d. In residue from neutralization of acid solutions
      (a) Soluble compounds.
      (b) Insoluble compounds.
    e. In mother liquor.
    f. In gases during drying of the fluoride.
  B. Alumina.
    a. In dust from calciner.
    b. In residue from neutralization of acid solutions.

VIII. Corrosion of apparatus.
  A. By vapor of HF.
  B. By solutions.
    a. Acid solutions.
    b. By neutral solutions.

Investigations Carried Out

I. Formation of HF gas from Aluminium Fluoride and steam. After assuring myself of the completeness with which the reaction $Al_2F_6+3H_2=OAl_2O_3+6HF$ is carried out when the products are removed, I tried the reaction at the temperatures given below with results as shown. The preliminary tests were run in an open crucible, (of platinum), at a red heat, the temperature tests in a pipe heated from the outside, a steam pipe connected. The steam and vapor were led into a copper beaker containing water, and the amount was determined by titration with normal alkali, phenolphthalein being the indicator.

Steam	Temperature	N. Alkali Used	Time
93.5 g.	100 C.	0.3 cc.	20 min.
30.0 g.	180 C.	0.0 cc.	20 min.
169.0 g.	300 C.	1.0 cc.	20 min.
95.0 g.	400 C.	16.2 cc.	16 min.

About 20 grams of fluoride were used each time; in the last case the outside of the tube was red hot while the Pyrometer showed only 400° C. (iron tube). Temperature was taken by a thermocouple of nickel-iron, calibrated with a Weston mill voltmeter.

This work shows that somewhere between 300° C. and 400° a real start was made in the evolution of the gas. What effect clay would have has not as yet been tried. This and some other tests I hope to make during the summer, and bring to the Congress.

II. Effect of HF gas on clay.

The only point tested as yet is that at 100° C. no sign of silica is to be found in the solution. At what temperature it does come over, and what effect if any steam will have, as also the speed of removal of the products of the reaction, have not been settled.

III. The absorption of HF by water.

In making these tests it was necessary to get as steady a flow of the gas as possible, and to do so I first used calcium fluoride and sulphuric acid, then aluminium fluoride and acid, then dilute hydrofluoric acid, and next sodium fluoride and acid, and last of all ammonium fluoride and acid. When running the gas into the tower to show the amount absorbed by the water and clay, titrations were made at intervals as shown below, showing at the same time the uniformity of evolution of the acid.

Length of interval	Alkali Used
15 min.	5.3 cc.
14 min.	5.2 cc.
12 min.	4.3 cc.
12 min.	6.4 cc.
10 min.	3.0 cc.
17 min.	5.3 cc.
12 min.	4.3 cc.
14 min.	3.4 cc.

It will be understood that these runs were made on one lot of ammonium fluoride and acid, air being blown through all the time, and water running slowly through the tower. The fluoride weighed 10 g., (48% NH_4F), was placed in a lead cup set in a bath of calcium chloride, at a temperature of 120 to 135° C. air running 19 cubic feet per hour.

A. In testing the effect of concentration of the gas, it was difficult to get acceptable results, for when slow air currents were used the acid seemed not to be delivered to the tower. The results obtained follow:

Time of Run	Cu. Ft. Air	Wt. of NH_4F	Alkali Used	Water per min.
1 hour	16.7	9.5 g.	48. cc.	20 cc.
1 hr., 5 min.	5.8	10. g.	35. cc.	20 cc.
55 min.	5.2	10. g.	17.5 cc.	20 cc.
1 hr.	24.	10. g.	41.0 cc.	20 cc.
1 hr.	approx. 40	10. g.	41.2 cc.	20 cc.
1 hr., 4 min.	19.3	10. g.	27.2 cc.	80 cc.
1 hr.	15.9	10. g.	32.4 cc.	8 cc.

The alkali used includes that required for the rinsings. These consisted of 500 cc of water poured through the tower in three lots. To test the completeness of the rinsings in the last case above, two subsequent rinsings were made in the same way, using the same amounts of water.

No. 1	6.0 cc alkali used.
No. 2	2.0 cc alkali used.
No. 3	0.8 cc alkali used.

Every time before a run, the tower was well rinsed by a stream of water for some minutes. This was repeated at the end of the run.

There was a notable change in the material titrated in the last run given above. That time the end-point was slow in coming, in the manner well-known to those acquainted with the titration of hydrofluosilicic acid. The longer time given in this case for the action of the acid upon the clay had its effect. Whether a longer time would have changed it to the aluminium fluoride, and how much of this effect was due to that material, I am not in a position to say. Certain it is that the end-point was always faster with the more rapid flow of water.

In the work outlined above, it is difficult to say how much of the HF gas if any, actually escaped. Frequent attempts to get the odor at the top of the tower gave rarely a trace of the smell, and I am coming to believe that very small amounts of the gas may be detected in that way, but in some previous work with a weighed amount of a titrated acid, titrating the acid caught I found that from 80% to 90% of the acid was caught. In this work just given, I could be certain of the amount of acid passed into the absorption tower, but I could not tell about the dilution of the gas.

C. Heating clay has the well-known effect of ending the property of slacking in water. It is also known that this treatment increases its solubility in acids, hence the clay for the tower may be benefitted by this treatment. The temperature varies for different clays, but those used in these experiments showed up well when heated to 300° C. or thereabouts.

The tower used has a depth of clay of about 8 inches. Size of lumps, through one-half and on one-quarter inch. Weight of clay, one pound.

IV. Not enough work has yet been done on the absorption of SiF_4 to be acceptable, but indications point to the rapid reaction of this gas with water, forming hydrofluosilicic acid, and a glass plate placed on top of the tower showed no sign of any action of fluorides or deposit of silica with the moisture condensing there.

V. Neutralization of Acid Solutions by Clay.

This has been well worked out in the Grabau process for the preparation of Aluminium Fluoride from Clay. (Richards; Aluminium, Third Edition, p. 173). This article points out the need of proper calcination of the clay if neutrality is to be obtained, which is necessary for the elimination of the silica; it is also necessary for the precipitation of the iron and titanium, and the freedom from action on vessels used in the concentration of the liquors.

If the solution is strong, (15% HF), the chemical action will heat it, and the action will be rapid; if weaker acid is to be neutralized it may be best to heat it. The solubility of the fluoride is much greater in the hot, which accounts for the ease of neutralization then.

So far as this process is concerned the elimination of the silica is not an important matter, as any left in would go off in the calciner later, but although half the iron and more than half the titanium have in my experiments been volatilized in the calcination, (allowing of course for the alumina from the fluoride as well as that from the clay), as much as possible should be precipitated in neutralizing the acid.

VI. Crystallization and drying of Aluminium Fluoride.

The solubility of the fluoride is so much greater at high temperatures that a solution which shows 25° Be. after filtering hot crystallizes enough fluoride over night to bring it to 7 or 9° Be. Refrigeration further reduces the solubility. While refrigeration may be used, evaporation in an open pan gives good results, the product being free from iron if the scrapers used to remove the crystals do not scrape too hard on the bottom of the pan. There is a layer of ferruginous salt next the pan which should not be disturbed. Some fluorine is no doubt lost here by hydrolysis, which may be reduced by running these gases to the tower where the acid vapor is recovered, and in other ways.

VII. Loss of fluorine.

To get an idea of the vapor pressure of solutions of hydrofluoric acid, a ten-gram sample was placed in a lead cup and air blown through at the following temperatures, the gas and air passing through water containing a known volume of normal alkali in a wooden cup. The excess of alkali was then titrated.

Temperature	Normal Alkali
14° C.	0.5 cc.
60° C.	0.4 cc.
75° C.	0.4 cc.
100° C.	0.5 cc.
102 to 109° C.	15.7 cc.

Time in each case ten minutes, except the last, which was between four and five minutes.

These results, with the absence of etching on glass placed on top of the tower, and the high recovery when the acid was volatilized and blown through the tower with a large excess of air, indicate the low losses of the gases. To what extent dusting would cause a loss I am not able to say. The dust itself would mostly be caught in the tower, but the solubility of the fluorides is low enough so that some of it would in all probability go along with the residue. Such a residue showed on analysis

Water,	11.5%
Silica,	70.0%
Ferric Oxide,	1.0%
Fluorine,	2.5%
Alumina (including that as Al_2F_6),	11.0%

The loss in the finished product is not really a loss, as it enters at once into the other office of fluorine in the aluminium industry. If, however, the product is to be used for the fused oxide, this fluorine is a loss and causes a loss of alumina also, the crystalized fluoride being formed on the side of a crucible when heated in a strong blast.

Corrosion.

One objection to the use of any method employing the fluorides or HF is the corrosion caused by these compounds. On the one hand let it be said that this property is the very reason why this process is available. On the other hand the vapor of HF does not corrode iron when no moisture condenses upon it, unless the corrosion occurs at or above a red heat. On this point I am not informed. Iron is therefore available as a construction material at the higher temperatures, and lead at the lower.

PHOSPHOROUS AND ITS COMPOUNDS STUDIED ESPECIALLY IN RELATION TO THE MANUFACTURE OF MATCHES

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Particularly important just now are the problems connected with the constitution of the igniting mixtures used for the heads of matches. Therefore, the following account of the principal varieties and derivatives of phosphorous, which have been used or proposed to be used in the match industry, is with much respect submitted to the Congress by the writer, together with some remarks upon the relative suitabilities of these products for the purpose, and a few suggestions regarding the characters to be sought in the ideal igniting substance for the match of the future.

From the date of Sauria's invention of the phosphorous friction match (1831) until six years ago, ordinary white or yellow phosphorous was pre-eminently the combustible body for match-heads; but Lorinser and other investigators, from 1845 onwards, pointed to the dangers attending its use; and since 1906 in most European countries this has been forbidden. Some countries (Denmark and Switzerland for instance) even earlier prohibited the manufacture of matches with white phosphorous in the compostions. Great Britain adopted prohibition in 1908 (8 Ed. *VII.*, 1908, ch. 42); and there can be little doubt that eventually every country in Europe will follow suit. This is, for the sake of the workers in match factories earnestly to be wished. United States also has formed a way to put a stop to the use of white phosphorous in the manufacture of matches by a prohibition tax placed upon their production after July 1, 1913. The horrors of the phosphorous disease, matchmakers' necrosis, or "phossy jaw," as it used to be called by the British operatives, have caused an incalculable amount of suffering; and we, of whatever race, owe it to our account with coming generations that in our time we should have stamped out the evil in every part of the civilized world.

White phosphorous was in early days thought to be as unmanageable as a man-eating tiger. Mixtures with diluents such as magnesia (Derepas, 1809), were kept in flasks or phials and withdrawn in small quantities at a time, upon splints, which were then ignited by friction. Later, after Sauria and his successors had shown how easily white phosphorous friction matches could be made, and after these products had long been in general use, the grave difficulty of necrosis presented itself: a difficulty yet being grappled with in countries where the use of ordinary phosphorous has not been discontinued. The striking parts of the heads of double-tip matches are stated unfortunately to contain extremely large proportions of white or yellow phosphorous; and it should be the aim of every maker to produce similarly excellent matches free from a particle of this risk-laden ingredient.

The dark red, or so called "amorphous," variety of phosphorous, discovered by v. Schrötter (1845), but, it would seem, previously tried by Pasch (1844), in the belief that he was working with an oxide, and during the fifties unsuccessfully essayed in strike-anywhere matches by British, French, and Austrian manufacturers, came chiefly to be used as is well-known, in the rubbing surfaces or rubbers, on the boxes of safety-matches. The last-named, by the way, have greatly increased in popularity of late years in Great Britain. The difficulties attending the employment of amorphous phosphorus in the heads of strike-anywhere matches have of late years been overcome to a considerable extent. The writer has not only examined good matches of Continental manufacture, with dark red phosphorous in the friction-heads, but has himself succeeded in making practicable red phosphorous strike-anywhere matches of quite presentable quality. The perils of mixing and milling match-compositions containing red phosphorous have for many years been unduly magnified, not to say exaggerated; and it is possible to prepare without danger mixtures containing reasonably small proportions of red phosphorous, which in the match-heads will not ignite explosively, nor burn with fierceness and irregularity.

Dark red phosphorous, when reasonably pure, is non-toxic, gives off no vapour or "fume," even at temperatures far above ordinary working and living conditions, and the temperatures required to ignite match-compositions containing it are considerably higher than those which cause the "firing" of white phosphorous compositions. The disadvantages of dark red phosphorus are its high price, and a tendency, shown in many commercial samples, to take up moisture and undergo partial oxidation. Many ways of "taming" amorphous phosphorus have been tried; the efforts have been in the directions of rendering less violent its reaction with potassium chlorate of modifying the temperature of its ignition, of rendering the material less hygroscopic, and of making it safer to handle in the factory. Mixtures of red phosphorus with zinc powder, sulphur, chalk, paraffin wax, zinc oxide and chalk together, borates and phosphates, or with flour and cork-dust, have been used by various inventors; boiling with aqueous solutions of metallic salts, and distillation, followed by filtration (for the removal of acidity, etc.) have also been suggested. The Schwiening method of introducing calcium plumbate into a match-composition containing red phosphorous, potassium chlorate, and other ordinary constituents, was in 1907 adopted in Germany, with some success, though the matches so made have not been free from severe criticism. It is contended that the calcium salt, in decomposing, produces lead peroxide, neutralizes the acid products of oxidation, and regulates the combustion.

The so-called "neutral amorphous phosphorous" of Caussemille Jeune et Cie and Roche et Cie (1909) is prepared by "treating by distillation and filtration ordinary amorphous phosphorous which has previously been well washed." These processes remove small quantities of white phosphorous, oxy-acids of phosphorous, or alkaline bases, if present; the product is stated to be without any basic or acidic reaction; and the use of such a preparation may undoubtedly diminish the risk of formation of hygroscopic compounds in a red phosphorus match composition.

Other varieties or derivaties of the element phosphorus are of different shades of red, from orange-tinted to scarlet, insoluble in carbon disulphide, just as is dark red phosphorus, more chemically active than the last-named inflammable in some instances at lower temperatures, and, so far as we know, non-poisonous.

The only one of these light red products known to the writer to be used in Great Britain is "Scarlet Phosphorus," or "bright red phosphorus," $(P_4)_2$ (?), discovered by Schenck (1903), but products of somewhat duller tints, similar to those obtained by Boeseken's (1907) and Zecchini's (1907) methods, are, it is believed, considerably used abroad.

Scarlet phosphorus is employed, in the United Kingdom, for the production of strike-anywhere or "parlour" matches, but not to a very large extent; and. although it yields very good matches, these, in the opinion of friends of the writer who are match manufacturers, strike less freely and yield more smoke than matches made with tetraphosphorus trisulphide, one of the class of compounds and derivatives next to be described, namely, the sulphides of phosphorus. Faraday (1818) was one of the first to prepare any of these bodies; Berzelius and later observers worked at the subject throughout the nineteenth century; in 1823 small quantities of sulphur and phosphorus, carefully fused together, were supplied in phials, in conjunction with sulphur-tipped splints, by which some of the mixture was withdrawn, to be kindled by friction; Puscher (1860) proposed without avail the use in match heads of sulphide of phosphorus instead of phosphorus: Bals (1896) suggested the employment of a fused mixture of the sulphur and red phosphorus: and finally, an examination of tetraphosphorus trisulphide, discovered by Lemoine (1864) led Sévène and Cahen to adopt this compound in the manufacture of French matches (Ger. and Eng. patents, (1898).

More than a dozen compounds of phosphorus and sulphur have been described or mentioned by Faraday, Berzelius, Böttger, Mitscherlich, and later investigators—P_4S (Berzelius, 1843); P_2S (Faraday, 1818, Berzelius, 1843); P_2S (Berzelius); terraphosphorus trisulphide, P_4S_3 (Lemoine); P_2S_3 (Serullas), P_3S_6, P_2S_4, or PS_2 (Seiler); pentasulphide, P_4S_{10} (Berzelius); P_4S_5 and P_4S_7 (Mai); P_8S_{11} (Dervin); P_3S_5 (Boulouch); PS_6 (Berzelius); and P_2S_6 (Stock and others); Helff (1893) considered that the existence of four of these compounds had been proved; P_4S_3; P_4S_7; P_3S_6 and P_2S_5. But Stock and v. Bezold (1908) and, corroboratively, Mai (1911), conclude that the existence of only three sulphides of phosphorus have been established: namely, tetraphosphorus trisulphide, P_4S_3, tetraphosphorus heptasulphide, P_4S_7, and tetraphosphorus decasulphide, P_4S_{10}. The trisulphide or so-called "sesquisulphide," is the chief phosphorus derivative applied at the present time in Great Britain to the manufacture of strike-anywhere matches. It is extensively used in Sweden and elsewhere on the Continent of Europe: exclusively in France: and very largely indeed in the United States of America. Non-toxic, pale yellow, soluble in carbon disulphide, inflammable at about the temperature of boiling water, readily workable in match compositions, yielding mixtures which do not give off injurious vapours during the manufacturing operations, and moderate in price, sesquisulphide of phosphorus has proved itself a useful and satisfactory substitute for the deadly phosphorus. The matches, if in a trifling degree less sensitive to friction than the white phosphorus products, are as good as can reasonably be desired; and their manufacture is at least humane.

Other preparations of phosphorus and sulphur containing the elements in proportions different from those in sesquisulphide have been suggested or tried in Europe, such as the products described by Wheelwright (1902), combinations of phosphorus with sulphur the phosphorus being in excess of that present in tetraphosphorus trisulphide; Johnson, for the Chemische Fabrik Griesheim-Elektron (1902), compounds stated to be the trisulphide P_2S_3, hexasulphide P_3S_6, and pentasulphide P_2S_5, with the addition of zinc oxide to prevent the evolution of sulphuretted hydrogen from the wet match-composition; Huch (1903), a preparation of sulphur and phosphorus obtained by treating red phosphorus with sulphur chloride, or with a solution of sulphur in the chloride; and Stahl and Nölke (1910), P_4S_{10}, prepared by heating to the fusing point a mixture of P_4S_3 with sulphur and described as separating from its solution in carbon disulphite in the form of yellowish plates. This body melts at 52° C., and at 128°-130° C. is converted into P_2S_5, insoluble in carbon disulphide.

Besides the foregoing sulphur-phosphorus preparations and very closely related to some of them, several compounds containing or consisting of metallic thiophosphites, hypothiophosphites, and pyrothiophosphites, have been introduced for match-manufacturers' use: such as the Griesheim Elektron Company's "sulfophosphit" (1902) a thiosulphite or hypothiosulphite preparation, in which are very intimately associated together sulphur, zinc, and phosphorus, stated to be obtained by uniting red phosphorus, sulphur, and metallic sulphites, in the required proportions: the product of Gartenmeister (1908) consisting of the pyrothiophosphite of antimony or other heavy metal; and Staier's compound (1912), made by heating red phosphorus, sulphur chloride, and a metallic sulphide to 65° C.

Oxygen compounds of phosphorus have also been tried. In the year 1898, Bohy, Gallay and Company proposed the use of metallic hypophosphites, such as the calcium salt in conjunction with bichromate of potassium and barium chromate; and the writer during the following year made on a fairly large experimental scale some quite good matches containing calcium hypophosphite in association with chromic acid.

The agent of the before-mentioned Griesheim-Elektron Company in 1903 patented a substance claimed to be phosphorus suboxide, P_4O. Whether the existence of a definite compound represented by this formula has yet been established, is, however, a debatable question, which Chapman, Lidbury, and Burgess (1899-1901) have answered in the negative, though Michaelis and v. Arend (1902) dispute their conclusion. Hydrides of phosphorus have not been forgotten, and have yielded encouraging results. Wheelwright (1906) proposed the use of solid phosphorous hydride (P_4H_2) or $P_{12}H_6$ and Castiglione (1907) followed suit. Later (1909), Wheelwright recommended the hydride P_9H_2, an orange red product obtained from $P_{12}H_6$ by the action of sunlight, or by exposure to a temperature of about 175° C. Many trials have been made with metallic phosphides, but the results obtained by the writer were not promising.

Lastly, a few organic compounds of phosphorus, or preparations in which the element is intimately associated with carbon compounds have been suggested. Examples are phosphorus phenylhydride, P_4H, C_6H_5 (Wheelwright, 1906); and certain mixtures of hydrocarbons, such as naphththalene, anthracene, and the like, with phosphorous (Bale, 1902).

The *desideratum* is still a combustible substance which will ignite at a temperature sufficiently but not dangerously low, which will be absolutely non-poisonous, will give off no injurious vapour or "fume," at any stage of the manufacture, and can be used with ease and safety in match works. It must mix evenly and well with the rest of the ingredients of a match-composition and without any disengagement of gas, should have no retarding effect upon the drying of the binding medium, and should yield a product as sensitive to friction as the best "double-tip" match that ever was made. The match must be liable neither spontaneously to ignite at any reasonable temperature, nor to be affected detrimentally by a damp atmosphere. In conclusion, the new and ideal match-product must be cheaper, either absolutely, or relatively to excellence of quality and the advantages provided, than anything now to be had.

SUR UNE METHODE NOUVELLE DE RECUPERATION des matières employées dans la fabrication de la soie artificielle au collodion. (Sulfhydrates alcalins)

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Depuis l'année 1884, époque à laquelle la Cte de Chardonnet déposait en France le brevet où fut décrit pour la première fois la méthode si ingénieuse qui permettait de préparer, par filage sous pression d'une solution de collodion, des filaments de soie artificielle, le procédé de Chardonnet étudié et perfectionné de toutes façons par les techniciens a pris rang, après combien de vicissitudes, parmi les procédés vraiment industriels.

Plusieurs Usines produisent *annellement* en Europe une quantité voisine de 3,000,000 kgs. de soie au collodion soigneusement dénitrée.

Mais des industries rivales sont apparues, capables de fournir des soies artificielles parfaitement vendables: le filage de la soie viscose et celui des solutions cuproammoniacales de cellulose sont aujourd'hui industriellement réalisés avec succès. A raison de la simplicité plus grande des réactions utilisées, de la récupération apparement aisée d'une partie des matières premières; de la suppression de l'alcool et de l'éther comme véhicules, on aurait pu considérer à priori comme devant devenir meurtrier pour l'industrie de la soie de Chardonnet, le développement de ces concurrents. En fait jusqu'aujourd'hui ces craintes apparaissent prématurées ou injustifiées. Pour des causes plutôt générales, sans doute, le prix de la soie au collodion s'est abaisée mais l'industrie de la soie au collodion ne paraît pas avoir été plus sensiblement affectée par l'apparition des autres soies que par ellemême, je veux dire par la prolifération des usines de soie au collodion. On en trouvera la preuve dans ces quelques chiffres comparatifs aux usines de soie les plus importantes de Belgique.

Nom de l'Usine productrice	Capital actions	Bénéfice industriel en 1911	
Soie artificielle de Tubize	2,000,000	2,101,868	Soi au collodion
Soie artificielle d'Obourg	1,500,000 frs	1,097,064 F.	
La soie Viscose (à Hofstave)	4,350,000	998,885	
Soie de Hal (Linkmeyer)	en liquidation		soie au cuivre ammoniacal

Ces chiffres attestent la vitalité réelle de l'industrie de la soie artificielle au collodion. En ce moment encore une usine nouvelle s'élève à Basècles avec le concours personnel du Comte de Chardonnet, inventeur impénitent aujourd'hui octogénaire.

Cette résistance du procédé au collodion, à la concurrence des autres méthodes tient sans doute à de multiples causes que l'object de cette note ne permet point de développer, mais on peut dire en passant qu'en fait, les soies artificielles au collodion au cuivre ou viscose représentent trois produits bien différents par leurs propriétés physicochimiques et qui sont spécifiquement appropriés aux usages variés des soies artificielles; la concurrence qui s'établit entre ces procédés est donc de nature spéciale. Quoiqu'il en soit la dépréciation d'ensemble du prix du kilo de soie artificielle[1] qui ne paraît pas devoir se relever notablement, l'augmentation récen te du prix de l'alcool qui a atteint en Belgique près de 100% depuis 1911 et celle du combustible, l'introduction imminente de lois sociales de protection ouvrière (suppression du travail de nuit des femmes) sont autant de facteurs appelés à infliger aux bénéfices de l'industrie de la soie au collodion une réduction progressive. Aussi a-t-on vu des usines adopter récemment des méthodes difficiles et coûteuses de récupération des matières premières et il ne paraît pas hasardé de prévoir que les fabriques de soie au collodion s'engageront progressivement dans cette voie.

Il faut placer au premier rang, quant à son importance économique, la récupération de l'alcool et de l'éther. La perte totale de ces produits représente selon nos calculs forcément approximatifs plus de 2.000 frs par jour par 100 klg. de soie produite. L'importante usine de Tubize (dont la production journalière tend vers 4.000 kgs) pratique notamment cette récupération partielle par absorption des vapeurs de la filature à l'aide d'acide sulfurique à 62 Bé et redistillation de cet acide malgré le grand inconvénient que présente cette méthode d'imposer un travail incessant et très considérable d'évaporation. D'autres procédés ont été proposés dans le même but dont on ne sait s'il sont réellement mis en oeuvre à l'heure présente. (voir Süvern: Die Künstliche Seide 3^e Ed. 912 Berlin Springer p. 125 à 158.) Moins conséquente mais d'application plus aisée et d'un réel intérêt économique peut être envisagée la récupération d'autres matières premières de la soie au collodion: acide nitrique, concentré et lessives sulfurées de dénitration. C'est de la récupération de ces derniers produits que nous désirons entretenir briévement les participants de ce congrès. Des nécessités momentanées nous interdisent d'exposer ici les résultats obtenus par nous dans la récupération de l'acide azotique pour laquelle du reste des brevets ont été pris de diverse parts; nous comptons y revenir bientôt. Bornons-nous à proposer ici les principes d'une *méthode nouvelle de récupération des sulfhydrates alcalins utilisés a la dénitration.*

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[1] Prix de vente de la Soie du collodion: en 1895, 60 frs.; 1900, 40 frs.; 1905, 20 frs.; 1910, 16 frs.; 1912, 14 frs.

Le filament de soie au collodion sortant des filières à haute pression est comme l'on sait, constitué par une nitrocellulose contenant environ 12% d'azote. Cette soie inflammable doit être dénitrée à l'aide de solutions convénablement étendues de sulfhydrates et de polysulfures alcalins ou alcalino-terreux; au cours de cette opération très délicate et qui mal exécutée peut compromettre la qualité du produit, une partie du soufre s'échappe sous forme d'H_2S, une autre se dépose à l'état libre dans le bain épuisé, une troisième enfin subsiste à l'état de polysulfure et de sulfhydrate non décomposés. L'azote nitrique pour sa part, passe à l'état de nitrite alcalin, d'ammoniaque et en faible quantité à l'état d'azote libre.

Les usiniers avaient donc à faire face au difficile problème d'évacuer des eaux résiduaires encore notablement chargées de sulfhydrates et de polysulfures alcalins, produits facilement décelables et hautement préjudiciables au régime des cours d'eaux; ils l'ont résolu notamment en faisant réagir dans des bassins spéciaux[1] les eaux sulfureuses alcalines avec les eaux acides ($xH_2SO_4 \div y\ H.NO^3 \div 2\ H_2\ O$) proveant du lavage des nitrocelluloses. Une neutralisation intervient qui s'accompagne d'un dégagement intense de vapeurs nitreuses et d'une précipitation abondante de soufre pulvérulent.[2] La réparation de celui-ci est favorisée par l'addition de sel d'alumine et la précipitation de l'alumine qui enrobde les particules de soufre; passé au filtre presse le sédiment peut être séché et vendu. Le prix qu'on en obtient ent à vrai dire fort bas.

Notre attention ayant été appelée par M. Denis, Directeur de la Fabrique de soie d'Obourg, sur l'avantage qu'il y aurait pour une usine de soie à retransformer ce soufre en sulfhydrate alcalin directement utilisable par l'usine; nous sommes par venus à résoudre le problème de la manière suivante.[3] La combinaison directe du soufre et de l'hyrdogéne fut étudiée d'abord par divers auteurs au point de vue qualitatif (Scheele, Davy, Correnwinder, Cossa, etc.) puis quantitativement au point de vue physicochimique par Hautefeuille (CR LXIV p 611) Pélabou (C R 1897 p. 35 et 686); Bodenstein (z f. physich Ch. 29 p. 314-333 1899) et Konowalow (Ch. Centrablatt (p. 657-1898 Bd II).

Les recherches de ces auteurs consistent à mettre en présence en vase clos du soufre et de l'hydrogène et à mesurer l'état d'équilibre et les vitesses de la réaction. Ils ne sont pas d'accord sur le point de savoir si la réaction est susceptible d'achèvement complet; en revanche tous ont constaté que la vitesse réactionnelle croît rapidement, comme d'usage avec la température.

Aucun ne parait s'être préoccupé d'étudier la réaction pratiquement et de rechercher s'il est possible de préparer des quantités notables d'hydrogène sulfuré par l'union directe de l'hydrogène et du soufre. La dépense théorique d'hydrogène étant d'environ $0.7m^3$ par kilog. de soufre, la recherche paraît à première vue devoir être écartée, étant donné surtout le prix élevé de l'hydrogène qui ne peut être ramené aujourd'hui en France ou en Belgique à moins de 0.25—0.30 fr par m3.

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[1] Voir D.R.P. 234672 cl. 85 c de la société anonyme fabrique de soie artificielle de Tubize (1911) d'après Süvern: loco citato p. 158. Voir aussi le brevet Belge antérieur de Leroy du 3 avril 1909.

[2] D'où la possibilité d'une récupération nitrique sur ces bassins.

[3] Voir Oct. Dony-Hénault Brevet Belge n° 17966 Sept. 1911.

Cependant l'avantage dominant de pouvoir éviter par l'emploi d'un réactif gazeux, tout transport et toute manutention de réactifs liquides, et surtout le *désir d'arriver a un procé dé excluant tout production d'eau résiduaire* nous ont fait rechercher s'il ne serait par possible d'arriver au même résultat; en substituant à l'hydrogène par un mélange gazeux riche en hydrogène et de prix de revient minime tel que le gaz à l'eau par exemple. Une expérience déjà ancienne de *Taylor*[1] montrant que le passage d'un courant de gaz d'éclairage dans une cornue contenant du soufre bouillant produit une forte quantité d'hydrogène mêlé de sulfre de carbone, était bien faite pour confirmer notre espérance car comme le dit *Taylor* c'est l'hydrogène libre du gaz qui agit dans ce cas et il peut être absorbé presque entièrement "nearly the whole."

En fait après avoir constaté que dans des tubes de deux mètres, chauffés modérement, un courant d'hydrogène passant sur du soufres peut réagir si complétement avec ce dernier que l'absorption du gaz sortant par une solution de soude peut être totale (H_1S ÷Na OH—Na SH ou H_2S÷2Na OH—Na $_2$S,) *nous avons vérifié la possibilité de substituer le gaz a l'eau* (50% H÷:50% CO *environ) a l'hydrogène* pour la production de l'hydrogène sulfuré au contact du soufre.

Le résultat peut être modifié en agissant sur la température; si celle-ci est maintenue au voisinage de 300-350°, la *formation concomitante du sulfure de carbone est pratiquement nulle.* Si au contraire on élève la température vers le rouge sombre, il se forme en même temps que l'H_2 S une certaine quantité de sulfure de carbone et'd'oxysulfure de carbone; si les gaz sont conduits au sortir de l'appareil dans des solutions de soude ou de sulfure sodique, le sulfure de carbone et l'hydrogène sulfuré sont absorbés simultanément; dans la solution absorbante apparaissent successivement du sulfure, su sulfhydrate, des sulfocarbonates et des polysulfures alcalins; quant à l'oxysulfure de carbone, il s'échappe avec les produits gazeux non utilisés dans la réaction; oxyde de carbone, et hydrogène résiduel; ceux-ci forment un mélange combustible dont la chaleur peut être utilisée pour le séchage préalable du soufre qui ne peut être introduit à l'état humide dans le générateur à hydrogène sulfuré.

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[1] Chemical News. Vol XLVII p. 145 1871.

Deus modes de travail différents sont donc possibles dans l'application de la méthode, l'un produisant à température plus basse de l'hydrogène sulfurè, pur, l'autre notablement plus rapide à cause de l'élévation de tempéture et de l'accélération réactionelle concomitante et fournissant de l'hydrogène sulfuré légèrement chargé de sulfure de carbone.

Les qualités requises d'une lessive de dénitration donnent un intérêt réel au second mode réactionnel. Le sulfure de carbone engendre en effet au contact des solutions absorbantes de sulfures alcalins du sulfocarbonate alcalin qui est un excellent agent de dénitration dont le prix élevé limite seul l'emploi.[1] Les liqueurs employées aujourd'hui pour la dénitration ont d'ailleurs une composition complexe; elles doivent être très riches en sulfhydrate, pauvres en sulfure et contenir une certaine quantité de polysulfures; la présence dans le liquide de deux ou troispour cent de sulfocarbonate ne saurait qu'accentuer sa valeur dénitrante.

Il nous est interdit d'exposer en ce moment la structure de nos appareils et les détails d'application de cette méthode, il serait au demeurant inopportun d'allonger cette communication dont le but principal est de signaler un principe nouveau susceptible de rendre service à l'industrie de la soie au collodion. On peut *en résumé se servir de l'hydrogène contenu dans le gazà l'eau (50%–53%) pour régénérer le soufre solide déposé dans les bassins d'eaux résiduaires des soieries, après* séchage préalable de ce soufre. *A une température supérieure* à 300°, *le soufre et l'hydrogène se combinent activement,* et les autres constituants du mélange gazeux ne réagissent sensiblement avec le soufre que si on atteint une température voisine du rouge sombre. *Le barbotage du courant gazeux à travers une solution constamment saturée de sulfure alcalin ou alcalino terreux fournit économiquement une liqueur saturée d'* H_2S *riche en sulfhydrate,* et pouvant contenir outre une certaine quantité de polysulfures, une faible quantité de sulfocarbonate soluble.

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[1] Voir *Piest* Die Zellulose. Stuttgart chg Euke 1910, p. 36.

Une telle liqueur peut être appropriée aux besoins de la dénitration de la soie.

La méthode permet donc, ***sans aucre production d'eau résiduaire génante,*** de substituer à l'achat des lessives de sulfhydrate dont la richesse totale en soufre ne dépasse pas 20% celui des sulfures solides et de préparer à l'usine même, le sulfhydrate à l'aide du soufre résiduaire des opérations antérieures.

UEBER DIE FRAKTIONIERTE ADSORPTION VON RADIUM-BARYUM-SALZEN UND ÜBER DIE FRAKTIONIERTE ELEKTRODIALYSE DER ERHALTENEN ADSORPTIONSVERBINDUNGEN

Von E. Ebler

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Es wurde früher[1] gezeigt, dass man mit bestimmten kolloiden Gelen die sich in einem bestimmten Grade des Wassergehaltes (Quellung) befinden, radioaktive Stoffe durch Adsorption anreichern kann, derart, dass nach erfolgter Adsorption die relative Koncentration der radioaktiven Substanz in der Adsorptionsverbindung wesentlich höher ist, als in dem unadsorbiert geliebenen Substanzgemisch. Es liess sich insbesondere zeigen, dass Kieselsäurehydrogele von der ungefähren Zusammensetzung 4 SiO_2 3 H_2O (—die also völlig staubtrockene Pulver darstellen, denn die Kieselsäurehydrogele sind schon unterhalb eines Wassergehaltes von 6 Mol. H_2O auf 1 Mol. SiO_2 staubtrockene Pulver—)[2] die radioaktiven Substanzen: Radium; Radioblei (Radium D, Radium E und Radium F); Niton (Radiumemanation); Uran X besonders stärk selektiv adsorbieren, sodass die kleinen Mengen der genannten radioaktiven Substanzen, die der Natur der Sache nach gewöhnlich mit einem vieltausendfachen Ueberschusse anderer Substanzen gemischt gegeben sind, durch wiederholte Adsorption sich fast quantitativ abscheiden und durch fraktionierte Anwendung des Verfahrens von den inaktiven Substanzen auch fast quantitativ trennen lassen. Die notwendige Trennung des adsorbierenden Kolloides von der adsorbierten radioaktiven Substanz erfolgte bei Verwendung von Kieselsäwre im Falle des Radiums, Radiobleies und des Uran X in einfacher Weise vermöge der Verflüchtigbarkeit der Kieselsäure durch Flusssäure als Fluorid, wobei die radioaktiven Substanzen in Form viel schwerer flüchtiger Salze zurüchkblieben.

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[1] E. Ebler u. M. Fellner. Ber. d. Deutsch. Chem. Ges. 44. (1911). 2332-2338 Zeitschrft f. anorgan. Chemie. 73. (1911). 1-30. E.Ebler. D. R. P. Nr. 243736· v. 7. III. 1911.—Zusatz. E. 17493. VIII. 21 g.v. 21. 11. 1911.

[2] J. van Bemmelen. Zeitschrft f. anorgan. Chemie. 13. (1897). 243.

Bei der Prüfung anderer Kolloide zeigte sich, dass nicht alle Kolloide in gleicher Weise ein selektives Adsorptionsvermögen für Radiumsalze besitzen und dass die Adsorption auch von der Natur des betr. Radiumsalzes abhängt. So adsorbieren z. B. 20% iges Gelatine-Gel. Acetylcellulose, frisch gefälltes Ferrihydroxyd nicht in so ausgesprochen selektiver Weise die Radiumsalze aus Radium-Baryumchlorid-Lösungen, wie z. B. die Kieselsäure. Dagegen zeigte Mangansuperoxydhydrat ein ganz ausgeprochenes Adsorptionsvermögen für fast alle Radiumsalze. Basisches Ferricarbonat zeigte ebenfalls ein sehr starkes Adsorptionsvermögen für Radiumcarbonat,sodass bei der Behandlung von Radiumsalzen, die einen überschuss von Ferrisalzen enthielten, mit Sodalösung alles Radium vom Eisen-Niederschlag zurückgehalten wurde.[1] Während die früher angegebene Methode zur Befreiung des adsorbierten Radiums vom adsorbierenden Kolloid nach erfolgter Adsorption aus der Adsorptionsverbindung flurch Verflüchtigung des Kolloides unter Zurücklassung der radioaktiven Salze naturgemäss nur auf solche Adsorptionsverbindungen angewendet werden konnte, die ihrer chemischen Natur nach zu verflüchtigen sind und bei dieser zweiten Phase des Processes weiter keine Anreicherung des Radiums möglich war, kann man solche Trennungen des kolloiden, vom adsorbierten nicht kolloiden Bestandteil, die auf der allgemeinen Eigenschaft der Kolloide beruhen, bei der Dialyse nicht durch gewisse Membranen zu gehen ganz allgemein auf alle kolloiden Adsorptionsverbindungen, deren einer Bestandteil ein Elektrolyt ist, anwenden und hat dabei noch den Vorteil, neben der fast beliebigen Auswahl der Kolloide auch die dialytische Trennung der radioaktiven Adsorptionsverbindung zu einer fraktionierten Dialyse gestalten zu können; denn fast stets durchdringen die adsorbierten Radiumsalze zu Beginn, bezw. Ende der Dialyse die Dialysiermembran in anderer relativer Koncentration als die gleichzeitig in der Adsorptionsverbindung etwa enthaltenen Baryumsalze.

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[1] Eine regelrechte " Fällung " des $RaCO_3$ lag nicht vor, denn die Radium-Lösung war so stark verdünnt, dass das Löslichkeitsprodukt des $RaCO_3$ nicht erreicht werden konnte.

So lässt sich z. B. die oben erwähnte Adsorptionsverbindung von basischem Ferricarbonat mit Radiumcarbonat durch Kochen mit der berechneten Menge verdünnter Salzsäure in Radiumchlorid und das kolloidale Sol das etwa der Zusammensetzung Fe $(OH)_2Cl$ entspricht spalten. Diese zwei Substanzen lassen sich alsdann durch Dialyse in bekannter Weise vollständig trennen. Rascher und besser in Fraktionen, teilen lässt sich die Dialyse wenn man sie durch Elektrolyse unterstützt, also z. B, das in den Kathodenraum dialysierende Erdalkalis Kationan Quecksilberkathoden entlädt, oder für seine Entfernung dadurch Sorge trägt, dass man die Kathode mit einem Strom verdünnter Salzsäure stetig umspült.[1] Durch gelegentlich rasch auszuführende Messungen der α-Strahlung eingedampfter Proben der Kathodenflüssigkeit und geeignetes Wecheseln der die Kathodenflüssigkeit aufnehmenden Gefässe, gelingt es leicht, die Elektrodialyse in geeignete Fraktionen einzuteilen.

Es hat sich weiter gezeigt, dass z. B. im Falle der Mangandioxyd-Radium-Baryum-Adsorptionsverbindung und der Kieselsäure-gel-Radium-Baryum-Adsorptionsverbindung es nicht notwendig ist, zwecks Ausführung der Dialyse das Kolloid in den Sol-Zustand überzuführen; man kann mitdemselben Erfolge in der beschriebenen Weise auch die im Gel-Zustande befindliche Adsorptionsverbindung der Dialyse bezw. Elektrodialyse unterwerfen. In manchen Fällen wirkt dabie das elektrokataphoretische Verhalten der Gele im Sinne der gewünscten Trennung und befördert dieselbe. So wandert z. B. die Kieselsäure nach der Anode, während das Radium sich zur Kathode begiebt. Aber selbst wenn die Kolloide, wie z. B. das Ferrihydroxyd das entgegengesetzte kataphorische Verhalten zeigen, also ebenfalls zur Kathode wandern, so lässt sich wie B. Schwerin[2] gezeigt hat, durch Auswahl geeigneter Diaphragmen die Trennung durch Kombinierung von katapho retischer Wanderung von Kolloidteilchen und Membranwirkung bewerkstelligen.

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[1] E. Ebler. Russische Patentanmeldung v. 23. Mai 5. Juni 1912 Nr. 53088.

[2] D. R. P. Nr. 181841. Nr. 233281. Nr. 239649. Nr. 241177.

A PLAN FOR ORGANIZED RESEARCH AND ANALYTICAL CHEMISTRY IN SUCCESSFUL CHEMICAL MANUFACTURING

By William C. Ferguson

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Introductory

The constant growth in efficiency in Manufacturing Chemistry is largely the result of organization that insures the orderly use of every varied talent required; and occupying a very important place in such organization is the fullest use of a research staff and of analytical chemistry.

When it is realized that these departments should investigate all new processes, constantly improve existing ones, correct and explain irregularities of current operations, invent new processes; that they should determine the valuation and exact composition of all raw materials and finished products, the fixing of yields, the necessary control of different stages of many processes, etc., etc., it becomes clear that if these constructive forces are to be used to the fullest it must be through the creation of an organization that will automatically cause every department in the organization to cooperate with the Research and Analytical branches.

The methods to be described for accomplishing this are the result of the writer's experience for many years in charge of the research work of one of the largest chemical works in America, with many plants in different localities, and also in charge of the research work of the largest electrolytic copper refinery in America.

Research Department

This department should investigate irregularities in current manufacturing; seek constantly to improve existing methods, and carefully consider new methods of promise as they arise.

Its duties should comprise: Investigating cheaper raw materials, new uses for products manufactured, new products, increased yields, greater purity of products manufactured, utilization of wastes, more efficient structural material, apparatus, etc., etc.

Great care should be exercised in the selection of the research staff which should embody all the varied talent and knowledge required in a wide field, and it is imperative here that only the very fit be retained as the achievements of this department will largely depend upon two factors—a highly efficient staff; and an organization that will, from every other department of the corporation, invite an automatic presentation of all questions requiring investigation.

The collective talent of this department should embrace thorough scientific education, especially in the principles of physics and chemistry; the power to imagine new processes, or causes of various irregularities of current manufacturing, combined with the ability to submit such ideas to the test of experimental proof; the habit of accurate observation and the skill to deduce from such observation the correct conclusion; and the quality of seeing right through all the unessentials to the one vital thing that counts. All of these qualities, diligently applied, together with a knowledge of manufacturing that will make all conform to practical conditions, are essential.

The department should have a manager with office organization and a properly equipped research laboratory with furnaces, filter presses, etc., where work can be carried on from a test tube scale to manufacturing in a large enough way to test practical difficulties and costs. There should be a Research Committee composed of the ablest technical minds of the organization, meeting regularly to consider and advise upon all important investigations.

Many questions presented to this department would be settled in debate negatively, but if experimental work be decided upon then, if the subject is new, the journal and patent literature bearing upon it should be abstracted and experiments usually begun upon a very small scale, increasing in size as warranted.

Each investigation should be made by a man selected on account of particular fitness and this man made responsible, but he should consult right along with other members of the staff whose knowledge or skill would be helpful, and progress made and difficulties encountered should be presented to the Research Committee at its regular meetings so that it could advise when necessary. At the conclusion of each investigation a detailed report should be made to the department. Exact estimate of cost should be made of each investigation in order to know the profit or loss in each particular case and also to estimate the value of the department as a whole.

The organization of this department should include:

(1) Systematic abstracting from the principal foreign and American journals and patents of all subjects of interest to the corporation; copies of these abstracts should go weekly to all who can use them, with instructions to study them carefully and to immediately advise the department of any subjects that seem to warrant investigation.

(2) Thorough abstracting from the literature in the case of new work undertaken, thus becoming familiar with all that has been published relating to the subject. Repetition of the work of others is thus saved, valuable suggestions received, and general knowledge of the subject enlarged.

(3) Systematic information should be constantly and promptly obtained of all records of imports and export and duties on all finished products and raw materials that would interest the corporation in connection with its current business or as suggesting new articles of manufacture.

(4) Pamphlets describing machinery, structural material, etc., are many years in advance of books upon identical subjects. A pamphlet library should be maintained in cooperation with the engineering department.

All of the above work of translating, abstracting, etc., should be in charge of one competent man, with assistants if necessary.

(5) The superintendents should make monthly reports for the Research department embodying all ideas of their own or their assistants that might in any way warrant

investigation. There is no doubt that valuable suggestions would be made through such a system thoroughly carried out that might otherwise be lost, and also that the plan would stimulate closer thought and observation concerning all the details in manufacturing.

(6) Members of the Research staff should visit all possible outside manufacturing plants with the object of acquiring knowledge that could be applied by the corporation to its own processes or organization.

(7) There should be, through proper connections, systematic prompt advices of all improvements in European practice that would be of value to the corporation.

(8) Salesmen should seek to understand the different processes and the various ways in which the company's products are used and also know what substitutes are used for the Company's products and such information should be reported to the Research Department by the Sales Department as deemed necessary.

(9) Certain research work might be undertaken by candidates for the degree of Ph.D. in universities, thus making these institutions of learning take a cooperative part in developing practical questions being considered by manufacturers. This can be done and the work be as strictly scientific as in the case of pure research and will also place certain students in contact with possible future employers.

ANALYTICAL DEPARTMENT

The Analytical Department, under the Chief Analytical Chemist, should control all work relating to sampling and analysis. So much depends upon prompt and accurate analyses that this department should occupy a high place in a rational organization. Its duties should comprise:

The analysis and sampling of all raw materials and finished products as well as such analyses as are necessary in the intermediate steps of some processes in order to insure proper control. It should furnish figures used to calculate yields and perform all the analytical work in connection with investigations, which often involves the necessity of inventing new methods. It should do all analytical work that will aid the Manufacturing, Sales, Purchasing, and Construction Departments, and cooperate with the Sales Department in investigating complaints. It should also pay strict attention to investigating and adopting better methods.

If a corporation has more than one laboratory, uniform methods of sampling and analysis should be used throughout. The selection of standard methods and the very complete written description of each should be under the immediate supervision of the Chief Analytical Chemist. Their accuracy should be proved always by analysing mixtures of known composition. The various precautions to be observed should be specifically and prominently outlined at the end of each scheme, together with the experimental data and all equations involved proving its accuracy.

These methods should be issued to the different laboratories and all chemists of the company required to strictly adhere to them, otherwise uniform methods with all their advantages, would be impossible.

The staff of the head laboratory should be organized into an analytical council holding weekly meetings, discussing at alternate meetings the company's standard methods of analysis and abstracts of promising analytical methods from the current chemical literature. These abstracts should be incorporated in the minutes of the meetings, copies of which go to each of the laboratories of the company. This sytem would automatically inform the company's chemists of the latest developments in analytical chemistry. All the important chemical journals should be promptly and systematically abstracted. These condensed abstracts should be typewritten on cards and filed under subject indices. They would prove of great value in investigating methods of analysis. All investigation work along analytical lines should be carefully written up, whether results are favorable or otherwise, and these reports sent to other laboratories of the company when desired. Any new methods suggested through the iterature or by any of the chemists of the company should be tried and where an improvement is found, incorporated in the standard methods.

The policy of the analytical department should be to give its members a broad acquaintance with all the work of the department by having a system of rotation, regularly changing the work of each so that, as far as possible, every man could take part in the great variety of determinations made. This would have the further advantage of protecting the company from any constant error into which one man may fall; and as an added protection, all the work should be systematically and independently checked by more exact or by different methods than those in daily use. Each man should be held strictly responsible for the work entrusted to him, his advancement depending upon himself, and he should be encouraged to become thoroughly familiar, through study and inquiry, with the theory and reasons involved.

As far as possible foremen and assistant foremen should make simple factory analyses and tests involving control of processes under them. Often a test can be made in less time than it takes to send the sample to the laboratory; of course such work should be systematically checked by the laboratory.

In order to estimate each man's capacity and to charge up the analytical work properly, the following system should be used: An analytical order should be made for each sample which comes to the laboratory and on the back of this order is recorded the amount of time spent by each chemist in making the analysis. When completed these orders should be filed under the various departments for which the work is done, and from them calculated a monthly statement of analytical charges, the material used being based upon the cost for the previous year. This system would make it a simple matter to note the progress of the analysis and the amount of work carried on by the different analysts.

The laboratories of the separate works should be strictly subordinate to the superintendents, except that all standard methods of sampling and analysis be standard methods of the company and superintendents and chemists should cooperate for their strict enforcement.

Salaries of chemists in this department should be standardized as far as possible, and promotions made to the following positions according to kind of talent: Works Chemist, Assistant Superintendent, Research Department as Research Chemist, the Head Laboratory as Chief or First Assistant. All men engaged should be informed of this system, hired on a month's trial, and only really promising men retained.

The following methods of advancing the efficiency of the department should be employed.

(1) Systematic visits to the different laboratories of the company by the Chief Analytical Chemist in order to see that the standard methods are being properly used and to pass on the general efficiency of all the company's laboratories.

(2) Occasional visits by the Chief Analytical Chemist to laboratories of other industries, in order to incorporate in the organization favorable developments made by others.

(3) Periodical meetings of the analytical chemists to promote cordial cooperation and to discuss specific subjects.

(4) The automatic exchange of chemists between the different laboratories to broaden the experience of the company's chemists.

(5) Monthly reports should be made by each laboratory of the company to the Chief Analytical Chemist, explaining all difficulties encountered in general work and also making suggestions for improvements in existing methods. This plan would make it possible for all the company's chemists to constantly and systematically cooperate and increase efficiency.

The organization of each of the laboratories of the company should conform to that of the head laboratory.

All laboratory buildings should be roomy, light, well ventilated, and equipped with all facilities required for accurate work. The efficiency and future of men is seriously impaired by unhealthful, discouraging surroundings.

The Head Laboratory and Office should have an extensive library and subscribe to all important periodicals. All works laboratories should at least have standard works of reference.

It would be important to have the Research and Head Analytical Laboratories in the same building, with the economy of having a library in common, and cooperation in many ways. This building should be located in one of the large works of the corporation, thus making available its mechanics for the various construction and repair work always necessary, together with the advantage of advice upon many practical matters from the works superintendents; there would result also the greater facility for consultation amongst members of the chemical staff.

The accuracy of balances and weights, of measuring apparatus, thermometers and hydrometers, should not be taken for granted but proved to be accurate by comparison with standards of known accuracy as often as required. All standard solutions should be checked by the head of the laboratory or his first assistant. All important determinations should be made in duplicate.

All clerical work and calculations should be checked.

Systems of weighing, manipulation, etc., devised to prevent errors, should be employed and rigidly adhered to, even in the simplest determinations.

CONCLUSION

The forms of organization described above should never be allowed to fall into the rut of dull routine, but the personnel of the men engaged in this work maintained at the very highest standard, and all the necessary plans as described carried out with enthusiasm, earnestness, and thoroughness. The personal cooperation of the men of this department with members of other branches of the organization would prove an important aid in maintaining interest in the work, and be mutually educating.

These departments should lead the way so strikingly as to be apparent to all; if mediocrity were tolerated, then this branch of the organization would be indeed far from the ideal that should be its governing spirit.

(Abstract)

THE ACTION OF POTASSIUM AMIDE ON THALLIUM NITRATE IN LIQUID AMMONIA SOLUTIONS

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The results of this investigation may be summarized as follows;

1. When a liquid ammonia solution of potassium amide is added to thallium nitrate likewise in solution in liquid ammonia a black precipitrate of thallous nitride is formed in accordance with the reaction expressed by the equation

$$3TlNO_3 + 3KNH_2 = Tl_3N + 3KNO_3 + 2NH_3$$

2. Thallium nitride dissolves readily in liquid ammonia solutions of potassium amide. When the ammono base is used in limited quantity a yellow solution is formed from which a compound of the formula $TlNK_2.4NH_3$ may be obtained in the form of beautiful yellow crystals.

3. Crystallized potassium ammono thallite readily loses successive portions of its ammonia of crystallization to form products of the composition represented by the respective formulas $TlNK_2. 2NH_3$ and $TlNK_2. 1\ NH_3$.

4. When thallium nitride is dissolved in excess of potassium amide, solutions are formed from which well crystallized products impossible of formulation as definite chemical compounds are obtained. These products are considered to be isomorphous mixtures of potassium ammono thallite with potassium amide or perhaps rather of potassium amide and the unknown thallium amide.

THE INFLUENCE OF POURING TEMPERATURE ON ALUMINUM ALLOYS

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The tensile strength of the light casting alloys of aluminum is greatly influenced by the size of the constituent crystals, or as the foundryman puts it, the "closeness of the grain." For any given composition, the finer the grain that can be produced, the stronger the metal.

These alloys follow the general rule that slow crystallization produced large crystals and rapid crystallization small ones. The speed of freezing is influenced by (a) the volume of metal in the casting and its relative dimensions, small thin castings freezing quickly and large, thick ones, slowly, (b) the temperature and heat conductivity of the mold (c) the temperature at which the metal is poured into the mold.

In practice (a) is fixed by the pattern from which the casting is to be made, and (b) is practically fixed by the ordinary use of green sand molds and dry sand cores, and is only altered by the use of "chills"—(pieces of metal placed in the mold at points where slow freezing would cause cracks or shrinks, and where the extra strength due to rapid freezing is essential to securing a good casting). The effect of these chills is mainly local as they are not used in sufficient quantity to greatly alter the speed of freezing of the whole casting. Hence the only variable is the temperature of pouring.

In making either commercial tests or scientific investigations of any physical property of cast aluminum alloys, the size of test piece, the composition of the mold and the pouring temperature should be recorded.

Table I shows the effect of the size of the bar—the alloy used being 8% Cu 92% Al—poured at 1300° F. in green sand.

TABLE I

Dimensions		Area of Cross Section	Tensile Strength lbs. per sq. in.
Flat	0.9" x 0.4"	0.36 sq. in.	16000
"	0.75" x 0.25"	0.19 " "	18000
Round	0.40" diam.	0.126 " "	20000
	0.45" "	0.159 " "	19000
"	0.50" "	0.196 " "	18000
"	0.75" "	0.442 " "	16000
"	1.00" "	0.785 " "	13500

Henry Souther (Brass World Vol. VII, P. 166), gives the following for an alloy of 16% Zn 2½% Cu 81½% Al.—all the bars being poured in the same mold.

TABLE II

Dimensions	Tensile Strength
Flat 1" x 1-8"	27000
1" x 1-4"	25700
1" x 3-8"	22200
1" x 1-2"	22800
1" x 5-8"	22400
1" x 3-4"	21200
1" x 7-8"	21700
1" x 1"	18800

There is evident necessity for a standard test bar. The best size is that specified by the Society of Automobile Engineers (Transactions Vol. 6, p. 520). This is ½" diam. at the breaking section, which is 2" long and filleted for at least ⅜" to a ¾" diam. threaded end. The use of chills or artificial methods of cooling is prohibited. The bar is to be tested unmachined in the breaking section, but with threaded grips. The American Society for Testing Materials specifies a similar bar but machined.

Machining bars and threading grips is expensive and impractical where large numbers of routine test are made. It is also unnecessary as the errors of measurement need not be great on a properly molded un-machined bar. We have tested thousands of bars on which the variation from the mean diameter of a $\frac{1}{2}''$ bar was not over 5-1000″ and in many cases it is less than 2-1000″.

We took 150 bars consisting of 75 pairs of bars cast in the same mold, the alloy being 12, and the pouring temperature 1300° F. Three sets of 25 companion bars were tested without machine or threading grips, one set was machined just far enough to cleap up and the grips threaded, one set had threaded grips but was not machined in the breaking section, the other set was machined in the breaking section but the grips were not machined or threaded. The results follow:

TABLE III

Set Number	Bars not machined or Threaded	Companion bars	
1	17830	18450	machined and threaded
2	18020	18460	threaded but not machined
3	17970	18790	machined but not threaded

It is plain that improvement due to more accurate measurement of the machined section, or to a straighter pull on the testing machine due to the use of threaded grips and ball and socket holders, is not enough to pay for the machining, therefore the tests that follow, are on bars as cast, and pulled in wedge grips.

The quantitative effect of pouring temperatures is shown by Table III, for an alloy of 8 Cu 92 Al., the standard Soc. of Auto Eng. Test bar, six in a mold, molded in green sand with gates the full size of the end of the bar, poured from a 1″ sprew at one end with a 1″ riser at the other.

TABLE III.

Pouring temp. deg. "F"	Tensile Strength lbs. per sq. in.
1200	20000
1250	19500
1300	19200
1350	18500
1400	18000
1450	17800
1500	17500
1550	17000
1600	16000

Table IV gives the averages for some fifty alloys poured cold and hot. The percentage of alloying elements is given in the column headed "Composition," the balance being aluminum containing 0.3% Fe and 0.2% Si as impurities.

TABLE IV.

No.	Composition	Poured Cold		Poured Hot	
		Prg. Temp. deg. F	Tensile strength lbs. per sq. in.	Prg. Tem.	Ten. Str
1	Pure Al.	1400	10500	1600	8000
2	2 Cu	1225	13800	"	11500
3	4 "	"	15500	"	13000
4	6 "	"	17600	"	14500
5	8 "	"	20000	"	15500
6	10 "	"	21000	"	16000
7	12 "	"	22500	"	17500
8	4 Zn	"	13000	1550	10000
9	8 "	"	17000	"	12700
10	12 "	"	21000	"	14000
11	16 "	"	24000	"	17000
12	20 "	"	27000	"	20000
13	24 "	"	30000	"	24500
14	28 "	"	33000	"	27500
15	32 "	"	35000	"	30000
16	36 "	"	37000	"	33000
17	3 Cu 3 Zn	"	17000	"	13000
18	7½ " 1 "	"	18000	"	14000
19	8 " ¼ "	"	20000	"	17000
20	8 " ½ "	"	20500	"	17000
21	3 " 6 "	"	19000	"	13500
22	7 " 3 "	"	19500	"	15500
23	6 " 5 "	"	20000	"	15000
24	2 " 10 "	"	23000	"	15500
25	4 " 8 "	"	23500	"	17000
26	5 " 10 "	"	24000	"	18500
27	7 " 9 "	"	25000	"	18000
28	3 " 12 "	"	26000	"	18500
29	3 " 15 "	"	28500	"	19500
30	3Cu 15Zn ½Mn	"	30000	"	20000
31	2 Cu 19 Zn	"	33000	"	25000
32	4½ " 15 "	"	32000	"	23000
33	2 " 22 "	"	36000	"	28000
34	2 " 25 "	"	37000	"	33000
35	1¾ " 30 "	"	42000	"	34000

TABLE IV—*Continued.*

No.	Composition	Poured Cold		Poured Hot	
		Prg. Temp. deg. F.	Tensile strength lbs. per sq. in.	Prg. tem.	Ten. Str.
36	3 Cu 25 Zn	1225	37500	1550	29500
37	2 Mn	1200	19000	"	18500
38	8 Cu ¼ Mn	"	20000	1500	17500
39	7 " ⅓ "	"	19000	"	16000
40	6 " ½ "	1250	18500	"	16500
41	4 " 1 "	"	16000	"	15000
42	8 Cu 2 Sn	1215	18000	1475	15750
43	5 " 3 "	"	16800	1500	15000
44	6 " 1 Ni	1300	18200	1600	14500
45	8 Cu ¼Ti	1250	19000	1500	18400
46	8 " ¼ Cr	1200	19500	"	15900
47	8 " ¼ Sb	1250	20000	"	17400
48	8 " ¼ Vd	"	20000	"	18500
49	8 " ¼ Cd	"	18600	"	15800
50	8 " ¼ Bi	"	18000	"	14000
51	4 " 4 Ag	1300	19700	1550	15400
52	8 " 1½Fe¾Si	1250	21000	1500	18000
53	5 Mg	"	20500	1400	20000

It will be noted that the bars poured hot average nearly 20% weaker than those poured cold. The notable exceptions are the alloys with 2% mn and with 5% Mg. The first has such a low elastic limit that it is seldom available for commercial use in castings. The alloys with magnesium oxidize so readily at high temperatures that it is essential to keep the temperature to which the metal is heated and which it is poured as low as possible to prevent burning out the magnesium and also to prevent getting a casting weak through the presence of dross caught in the metal.

The 5th alloy in the table, that with 8% Cu is the one most used for casting, easily 90% of all cast aluminum being of this alloy. The 11th, 15th, 30th, 31st, 35th, 43rd, 44th, and 55th, also find some commercial use, but a discussion of their relative values is outside the scope of this paper.

The addition of small amounts of Mn, Ti, Fe, or Sb to the 8% Cu alloy increases the strength when poured hot, while Ni, Cr, Cd, or Bi seem to be without much influence. Unfortunately, as far as our tests have gone, the elements which give increased tensile strength on hot pouring tend to cause brittleness and decrease the resistance to impact. The discussion of these points also lead us too far afield.

The most progressive foundries are now pouring all aluminum castings under strict pyrometric control, the temperature chosen for each particular casting being the lowest at which the mold will fill and at which the metal will still not freeze quickly to give up air trapped in pouring, which causes blow holes.

Many published investigations on aluminum alloys have given results far below the real value for tensile strength on account of hot pouring, or else due to irregularities in pouring temperatures, the results are ragged.

Souther's results, quoted in Table III, the work of Lane on magnesium as a deoxidizer in aluminum (Castings, Feb. 1911, p. 164). Portevin's work on Aluminum Zinc, (Revue de Métallurgie, Sept. 1911, p. 271), Simpson's work on the same (See Ewen & Turner) Journ. Inst. Metals IV, p. 151) all run low at least in spots from this cause.

The figures given for Al Zn cast in a graphite mold by Bancroft (The Foundry, Feb. 1910, p-268) are about the same as we get for green sand. Bancroft's pouring temperatures were controlled, and were as low as practical. His bars however, were larger than ours and the extra bulk of metal compensated for the chilling by the graphite mold.

Curry & Woods (Jour. Phys. Chem. Vol XI, p. 461) get higher results on Al Cu than are obtained under the conditions of our tests, in green sand with a $\frac{1}{2}''$ diam bar, as they used a graphite mold and a bar of half the cross-section of ours. They too, poured cold.

In the classical work of Carpenter & Edwards on the alloys of Aluminum & Copper (8th Rept. Alloys Res-Comm., Inst. of Mech. Eng.) they recognize (Collected Researches—Nat'l. Phys. Lab. Vol III, p 125) the influence of pouring temperatures, and say they pour as cold as possible, but their low results (p-212) for alloys above 4% copper show that their method of judging temperatures by the eye was not adequate. They drew the erroneous conclusion that the tensile strength did not increase with increasing copper above 4%, and the error was doubtless due to disregard of pouring temperatures.

Rosenhain and Lawtsberry (Coll. Res.-Nat'l. Phys. Lab. Vol. VII) in their work on Al-Cu-Mn, cast their bars at a moderate temperature (p-156), but really determined the pouring temperature on only one alloy (p-162) finding hot pouring detrimental on that.

Where any of these workers have taken the pouring temperatures, they have used platinum thermocouples in protecting tubes. The lag with this method is considerable, and we have found that base metal couples or "fire rods" of the welded end, rod, and tube type essential for quick readings. Some makes of pyrometer couples are too readily corroded by the aluminum, but we find the "Advance" fire rod—a cheap base metal couple—to stand up against this corrosion remarkably well.

We use the Fahrenheit scale simply because twenty-five degrees too high a pouring temperature would mean about the same to the average workman in any scale, and by using the Centigrade scale it would be more difficult to get him to pour so near the temperature he was told to use, as with the Fahrenheit.

ACTION DES MÉTAUX ALCALINS SUR LES CARBURES BENZÉNIQUES

PAR LOUIS HACKSPILL

Versailles, France

Dès 1865, faisant agir le sodium sur le benzène vers 200°, Lauth[1] signale un dégagement d'hydrogène, et un corps brun impossible à séparer de l'excès de sodium, il pensa que ce corps devait être du "phénylure de sodium." Schuteznberger[2] reprenant cette expérience en 1822, remarqua que le métal alcalin devenant spongieux, qu'il se formait un carbure solide (probablement du diphényle) et une masse brune contenant 92,2 pour 100 de carbone, et 4,3 d'hydrogène et 3,4 d'oxygène. D'autre part Berthelot a observé que le potassium et le sodium sont sans action sur le benzène convenablement purifié, même à son point d'ébullition. Cependant si l'on opère en tube scellé, il se forme très lentement vers 150° une masse noirâtre qui semble être un mélange de plusieurs composés.

Avec le caesium, la réaction commence à froid, il y a donc des chances pour qu'elle soit moins complexe.

L'expérience doit être réalisée dans le vide la plus parfait. Le métal puis le carbure sont introduits par distillation, et le tube qui les contient, séparé ensuite à la lampe. La tension de vapeur du benzène est assez grande à la température ordinaire pour permettre la rapide condensation de quelques centimètres cubes de ce liquide par un simple refroidissement à 80°. Si l'on abandonne le tube scellé ainsi préparé à une température de 15 à 20°, la surface du métal se ternit, puis redevient brun foncé; au-dessus du point de fusion (28°, 25), l'attaque est plus rapide surtout si l'on agite, ce qui a pour résultat de diviser le caesium en une multitude de petits globules qui ne se rassemblent plus. Il faut cependant malgré cette précaution deux ou trois jours pour transformer intégralement deux grammes environ de métal en une boue noire, assez dense, qui tombe au fond du tube. Aucun gaz n'est mis en liberté dans cette réaction. On peut séparer le composé noir formé du liquide surnageant par une série de décantations et de lavages au pentane sec. On chasse ensuite ce dernier par un courant d'acide carbonique. Le corps ainsi obtenu est amorphe, chauffé dans le vide ou dans le benzène il se transforme rapidement en donnant un produit résineux. Il brule spontanément à l'air avec une flamme fuligineuse. L'eau et l'alcool le décomposent à froid en donnant du diphényle. Par oxydation lente, par exemple à l'air sous une mince couche de benzène, il se transforme en un produit jaune extrêmement dangereux, car c'est un explosif aussi sensible que l'iodure d'azote Chauffé dans l'acide carbonique, le composé organométallique noir se décompose avec une série de petites détonations, sans qu'il soit possible de constater la formation de benzoate de caesium. Plongé dans le chloroforme, il produit une violente explosion, le tétrachlorure de carbone semble être sans action ainsi que l'éther et le pentane.

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[1] Lauth Bull. Soc. Chim. t. IV page 3 (1865).

[2] Schutzenberger Bull. Soc. Chim. (2) 37 p. 50 (1882).

Après bien des essais infructueux une analyse grossière a pu être effectuée de la façon suivante: La préparation était faite comme il a été dit plus haut, mais dans un petit tube en U dans lequel le produit obtenu était lavé plusieurs fois au pentane, séché à l'acide carbonique puis pesé. Après l'avoir soumis à l'action de la vapeur d'eau dans le vide pendant plusieurs jours, le tube était lavé avec beaucoup de précautions, séché et pesé, le caesium dosé dans les eaux de lavage à l'état de chlorure. Cette analyse a donné 65,34 pour 100 de caesium, nombre se rapprochant de 63,33 qui correspond à la formule C_6H_5Cs[1] laquelle est rendue très admissible par la formation de diphényle et de caesium au contact de l'eau. On pourrait objecter cependant qu'il n'y a aucun dégagement gazeux pendant l'action du caesium sur le benzène, bien que la substitution de Cs à H implique la mise en liberté d'un atome d'hydrogène:

$$C_6 H_6 \div Cs = C_6H_5Cs \div H$$

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[1] Le sodium phényle C_6H_5Na a été préparé par l'action du sodium sur le mercure diphényle $(C_6H_6)_2$ Hg; Acree—Amer. Chem. Journ. 29—5 (1903).

On peut expliquer ce fait en admettant que l'hydrogène naissant se fixe sur le noyau benzénique pour donner des carbures plus hydrogénés tels que:

$$C_6H_8,\ C_6H_{10},\ C_6H_{12}$$

La réaction complète serait donc de la forme:

$$3\ C_6H_6 \div 2\ Cs = 2\ C_6H_5Cs \div C_6H_8$$

Il n'a pas été possible de séparer sur quelques centimètres cubes de mélange, le benzène de ses hydrures. On ne peut que constater la différence entre ses constantes physiques et celles du benzène pur. C'est ainsi que dans une expérience le point de fusion a été abaissé de 0°4 et que l'indice de réfraction passe de 1,50 à 1,52.

Le rubidium se comporte d'une façon tout à fait comparable à celle du caesium vis-à-vis du benzène, mais la réaction est encore beaucoup plus lente. Il a fallu chauffer une dizaine de jours à 70° pour obtenir un décigramme d'un produit analogue au caesium phényle. On a pu également substituer le toluène au benzène sans modifier les résultats apparents de l'expérience, mais les composés formés n'ont pas été étudiés.

En résumé, les métaux alcalins attaquent le benzène à des températures d'autant moins élevées que leur oxydabilité est plus grande. Avec le caesium cette température est suffisamment basse pour que la réaction soit simple, elle donne vraisemblablement du caesium phényle

$$C_6H_5Cs$$

qui se décompose en présence de l'eau en déphényle et hydrate de caesium.

POTASH, SILICA AND ALUMINA FROM FELDSPAR

By Edward Hart

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In a study of the commercial utilization of feldspar which I undertook several years ago, it soon became evident that the potash alone would not pay the cost of extraction. This is the cause of the commercial failure of all the methods heretofore proposed. It is necessary, therefore, to separate and put into marketable form the other constitutents—silica and alumina—if our method is to be successful.

With this purpose in view I have finally worked out the following process which gives good prospect of commercial success:

The feldspar chosen should contain not much less than 12% potash. Spar of this quality can be obtained in quantity, but one of the pitfalls inventors must avoid is the expectation of getting spar containing the theoretical 16.9% of potash. The spar mixed with the proper amount of potassium sulfate and carbon is fused. The carbon added is so regulated that the resulting slag contains a considerable proportion of sulfids. This has the double advantage of saving a part of the sulfur, disengaged as hydrogen sulfid on dissolving in acids, which aids, also in the complete decomposition by breaking apart the particles as it is given off. Experiments show that if a colorless slag is obtained of even higher alkali content it is much less easily decomposed by sulfuric acid.

The slag so obtained must be very finely pulverized and treated in closed vessels with dilute sulfuric acid leaving behind a very pure silica which only needs washing and ignition to yield a marketable product fitted for the potter's use or for the manufacture of sodium silicate.

The solution contains potash alum and any small amounts of other metals such as iron, manganese and soda as sulfates. Lime is inadmissible, as the sulfate forms crusts on evaporating.

The solution on cooling gives at once crystals of alum, which washing with a little water and centrifuging renders marketable.

Any iron present remains as ferrous sulfate in the mother liquor. Alum, however, is marketable only in limited quantity and must be for the most part, converted into its constituents, aluminum and potassium sulfates. This is easily done by adding to the solution in a closed vessel potassium sulfid in slight excess when aluminum hydroxid mixed with a little sulfur precipitates in a form easily washed. This is dissolved in hot sulfuric acid, run through a filter and allowed to solidify. The potassium sulfate is obtained by evaporation.

Each ton of feldspar (12% K_2O) should yield

444 lbs. K_2SO_4
2040 lbs. Commercial Aluminum sulfate (18% Al_2O_3)
1300 lbs. SiO_2.

ALLOYS OF COBALT WITH CHROMIUM AND OTHER METALS

By Elwood Haynes

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As in organic nature, certain animal and vegetable forms have undergone modifications, and thus, as it were, fitted themselves to live in a new environment, so it has been found possible in certain instances to form new metallic combinations which are practically immune to the natural conditions that exist on the earth at the present time. A few of the rare metals, such as gold, silver, and the metals of the platinum group, are found native, but the commoner heavy metals are nearly always found in the form of oxides or sulphides.

For a number of years I have made experiments with a view to finding certain metallic combinations or alloys which would not only resist oxidation and other harmful influences, but would also possess valuable physical properties, which would render them fit for special services. The first decisive step made in this direction, was the discovery of an alloy of nickel and chromium in 1898. The properties of this alloy have already been described in a previous paper. Immediately following the discovery of the nickel-chromium alloy, I produced an alloy of cobalt and chromium. This has likewise been described in the previous paper, but the range of proportion between the cobalt and chromium is so great, and the combination is modified to such a marked degree by the introduction of other substances, that I have felt justified in reading another paper on this subject, describing more fully my researches in this particular direction.

As early as 1907 and 1908, I made alloys or combinations of cobalt, chromium, and tungsten; cobalt, chromium, and molybdenum; and cobalt, chromium, tungsten, and molybdenum. I have made alloys of cobalt and chromium containing zirconium, tantalum, throium, titanium, vanadium, etc. I have also added to the cobalt-chromium alloys, the non-metallic elements, carbon, silicon, and boron. Some exceedingly interesting results have been obtained from these various combinations, and while further investigation is necessary in order to fully determine their chemical and physical properties, a number of them have shown interesting economic possibilities.

The preliminary fusions were made in graphite crucibles by means of a furnace operated by natural gas. I was later obliged to use crucibles of a special composition, not only to avoid the contamination of the metal by carbon from the crucible, but also because they proved more reliable under long-continued heating, than those made of graphite.

The metal tungsten alloys readily with chromium and cobalt in all proportions. When added in small quantity to the cobalt-chromium alloy, it seems to have little influence on the properties of the combination, but if the proportion rises to 2% or 3%, a notable effect is produced. Generally speaking, the cobalt-chromium alloy becomes harder and more elastic, especially if it contains a small amount of carbon, boron, or silicon.

The following experiment shows the effect of melting the alloy in a graphite crucible: 90 grams of cobalt, 6.3 grams of tungsten, 18 grams of chromium, together with a small quantity of calcium silicide, were introduced into a graphite crucible. The resulting alloy was very hard, and the crucible much eroded on the inside. The bar could be slightly flattened at one end, and after being made into a cold-chisel, showed remarkable qualities. It would not only scratch glass, but also quartz crystal. It was quite tough at ordinary temperatures, and would cut small chips or shavings from a piece of STELLITE. At a bright yellow heat it showed signs of fusion, and became covered with a skin of oxide.

An alloy was made by melting the following in a special crucible: cobalt rondelles 80 grams, chromium 20 grams, tungsten 7 grams, calcium silicide 10 grams, calcium carbide 5 grams. As soon as the above were melted, the crucible cover was removed, and 15 grams of an alloy of cobalt and boron were introduced. The crucible lid was then replaced and the heating continued. A heavy, thick slag formed, which was removed before pouring the metal. The resulting bar was very hard and *elastic*, but only drew slightly under the hammer, and then broke. A cold-chisel made from the cast metal cut iron readily. The bar was broken up and remelted with about one-third of its weight of an alloy of cobalt, chromium, tungsten, and carbon. The result was a fine-grained alloy which was very *elastic*, and would draw out to a considerable degree under the hammer without checking. It's elastic limit must have been very high, since when it broke, the pieces were thrown violently.

Taking the alloy of chromium and cobalt as a basis, and holding the proportion of chromium at 15% of the entire mixture, it was found that the alloy gradually increased in hardness with the percentage of tungsten. When the quantity of tungsten rises to 5%, the alloy becomes distinctly harder, particularly when forged under the hammer. When the tungsten reaches 10%, the metal still forges readily, and a tool formed from the alloy takes a fine cutting edge. This alloy is suitable for both cold-chisels and wood working tools. When the tungsten rises to 15%, the metal can still be forged, but great care is necessary in order to avoid checking. This alloy is considerably harder than that containing 10% of tungsten, and is excellent for cold-chisels. When the tungsten rises to 20%, the alloy is still harder, and can be forged to a small extent. It makes good lathe tools for cutting steel and other metals at moderate speeds. When the tungsten rises to 25%, a very hard alloy results, which cannot be forged to any extent, but casts readily into bars which may be ground to a suitable form for lathe tools. These tools have shown great capabilities, particularly for the turning of steel, since they are very strong, and retain their hardness at speeds which almost instantly destroy the cutting edge of a steel tool. The tungsten may be still further increased to 40%, and the alloy will retain its cutting qualities, and for turning cast iron, this alloy answers even better than that containing 25%. When the tungsten reaches 40% or more, the alloy becomes so hard that it will not only scratch glass, but will readily scratch quartz crystal. A small drill made of this material, drilled a hole through the wall of a glass bottle without the addition of any liquid or other lubricant. A $\frac{3}{8}''$ square cast bar, when ground to a suitable edge, was set in a tool-holder attached to a lathe. The workman who had operated the lathe, had been able to turn to form 26 cast iron wheels in 10 hours with a steel tool of the same size. The STELLITE tool turned 49 of these wheels to form in the same time. The steel tool was ground 50 times during the operation, while the edge of the STELLITE tool was dressed slightly by a carborundum whetstone, after its day's work was completed. A set of steel cutters, placed in the boring head of a cylinder-boring machine, were able to bore from 26 to 28 holes in 10 hours. These cutters were replaced by others made of STELLITE, which performed the work in 3 hours and 20 minutes, or a little more than $\frac{1}{3}$ the time. Not only was the speed of the mill doubled, but the feed also, and notwithstanding this severe ordeal, the STELLITE cutters were only slightly worn, while it would have been necessary to re-grind the steel cutters at least two or three times for the same service at slower speed. Some remarkable results were obtained in the turning of steel on the lathe. For example, a cylindrical bar of annealed nickel-chrome steel, about $2\frac{1}{2}''$ in diameter, was placed in a lathe and turned with a steel tool at about as high a speed as the steel would permit without "burning." The steel tool was then replaced by one of STELLITE, and the speed at the same time increased to $2\frac{2}{3}$ its former speed. The STELLITE tool retained its edge under these severe conditions, and produced a shaving weighing $1\frac{2}{10}$ pounds in $\frac{1}{2}$ minute Just what the effect of the alloy will be in machine shop practice, is at present somewhat difficult to determine. In my opinion, however, it will not fully supersede high-speed steel in the machine shop, but in cases where rapid work is the main consideration, it will doubtless replace high-speed steel.

When molybdenum is added to a 15% cobalt-chromium alloy, the alloy rapidly hardens as the molybdenum content increases, until the content of the latter metal reaches 40%, when the alloy becomes exceedingly hard and brittle. It cuts keenly and deeply into glass, and scratches quartz crystal with ease. It takes a magnificent polish, which it retains under all conditions, and on account of its extreme hardness, its surface is not readily scratched. When 25% molybdenum is added to a 15% chromium alloy, a fine-grained metal results, which scratches glass rather readily, and takes a strong, keen edge. Its color and luster are magnificent, and it will doubtless find a wide application for fine, hard cutlery. It cannot be forged, but casts readily, and its melting point is not abnormally high.

If carbon, boron, or silicon be added to any of the above alloys, they are rendered much harder, though their effect is not always desirable, since they tend to render the alloys more brittle.

If either tungsten or molybdenum is added to a cobalt-chromium alloy containing 25% of the latter metal, the hardness of the alloy is rapidly increased. When the percentage of tungsten, for example, reaches 5%, the alloy can be readily forged, and forms an excellent combination for wood-cutting tools, such as chisels, pocket knives, etc. When molybdenum is added to the same mixture of chromium and cobalt, much the same effect is produced, though, generally speaking, a smaller quantity of molybdenum is required to produce a given increase in hardness. In some instances I have found it advisable to add both molybdenum and tungsten to the cobalt-chromium alloys. Generally, the color and luster of these alloys, after polishing, are magnificent, and they seem to resist atmospheric influences equally as well as the binary alloy of cobalt and chromium.

THE REDUCTION OF SOME METALLIC CHLORIDES BY SODIUM

By Matthew A. Hunter

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The affinity of sodium for chlorine has been used from the earliest times in the history of modern chemistry as a means of separating other metals from their combinations with chlorine. If these metallic chlorides maintain their solid condition at a temperature approaching a red heat, the reaction may be carried out in an open crucible, by simply heating the metallic chlorides and sodium together. The reaction when once started is carried immediately to a conclusion by the large amount of heat liberated by the first reduction. If however, the metallic chlorides are liquid at ordinary temperatures, or liquefy below a red heat, the vapor pressure of the chloride becomes considerable before reduction is begun, and some or all of the chloride is invariably lost.

It becomes necessary under these conditions to bring about the reduction within an enclosed space in order to prevent an unnecessary loss of material and also to conserve the heat of the reaction.

This method of procedure was used by Nilson and Petterson[1] in the reduction of titanium chloride and beryllium chloride, and by Krüss and Moraht[2] in the reduction of potassium beryllium fluoride by sodium.

The results of these experiments demonstrated the value of the method employed, but the amounts of material used in the reaction were so small that the metal was obtained as powder in a state of fine division, and not as a coherent metallic material. Further, since the metals titanium and beryllium are difficult to melt, no solid metal has ever been obtained from these finely divided powders.

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[1] Pogg. Ann. (2) 1878; Berichte 11. 381. 1878.

[2] Liebig's Annalen 260. 161.

In these pages it will be shown that the method of Nilson and Petterson has been so extended that the metals titanium and beryllium have been prepared in the metallic condition. Further, this method of reduction has been applied to the reduction of the liquid chlorides of carbon and silicon with however, less satisfactory results. Mention will also be made of an attempted reduction of neodymium chloride.

APPARATUS USED FOR REDUCTION

Two bombs were constructed from a solid piece of forged machine steel; a smaller one for preliminary investigations on small quantities of material, and a larger one, of ten times the capacity of the smaller, for those reductions which were found to proceed satisfactorily in the smaller bomb. The small bomb was made by boring a 1½″ hole in a cylinder 5″ deep and 3″ in diameter. This cylinder was provided with a flange 4″ in diameter and a lid 2″ deep which was fitted over the cavity in the cylinder. The bomb was maintained airtight by an intervening gasket of copper, which was pressed by hydraulic pressure into grooves in the cylinder and the lid. The lid was maintained in position by a steel yoke fitted over the flanges and pressing on the lid by means of a ¾″ bolt, five inches in length.

The larger bomb had an outside depth of 6½″ and an inside depth of 5″, and outside diameter of 4″, and an inside diameter of 3″. The flange at the top was 5″ diameter. The lid, which was 2″ in depth, was compressed upon the lower cylinder as before, with an intervening copper gasket, and maintained in position by six stout braces, 1½ x 1¾″ cross section and 6″ long. Each of these braces were bolted down by ¾″ bolts, 3″ in length. This bomb was calculated to withstand a total internal pressure of 80,000 lbs.

REDUCTION OF TITANIUM TETRACHLORIDE

A preliminary report on the reduction of titanium tetrachoride[1], has already been presented by the author; but a brief mention of it need therefore be given here.

Titanium tetrachloride prepared by the chlorination of tita-

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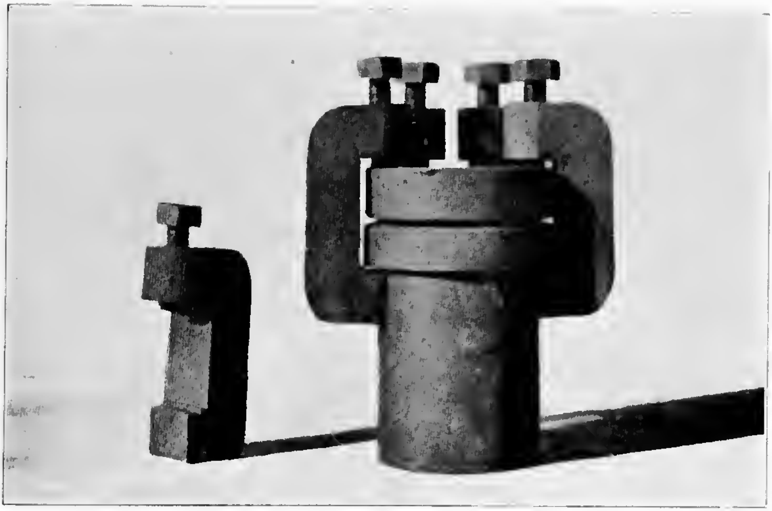
[1] J. Am. Chem. Soc., 32, 331 (1910).



nium carbide was purified by repeated distillation to remove other chlorides, and by shaking with mercury and sodium amalgam to reduce the last traces of chlorine. The water white, liquid chloride thus obtained was reduced with sodium, and a good yield of metallic titanium was obtained. The preliminary experiments in the small bomb gave most of the metal in the form of a gray powder and some of it in the metallic condition, in the form of rounded globules about the size of a pin head. When the reaction was transferred to the large bomb almost all of the metal produced was found in the metallic condition. About 100 grams of titanium were produced in each experiment, and of this amount, about 70% was in the form of metallic beads. This metal contained no trace of sodium, and only a faint indication of iron. Analysed by boiling in HCl and pptating with NH_4OH, it gave 99.9% Ti.

By dissolving in $KHSO_4$ and precipitating by boiling the solution, 100.2% of Ti. was found. The smaller pieces of the metal possessed a considerable degree of malleability. The larger pieces were hard and brittle when cold, but when raised to a red heat, they could be readily forged with some superficial oxidation into short rods. A regular bead of 12 grains' weight yielded a rod about six inches long, on careful hammering. The melting point of this rod was found by passing current through[1] it, in as perfect a vacuum as could be maintained, and observing the temperature of the rod by a Wanner pyrometer. It was found to be between 1800° and 1850°; certainly not higher than the latter value. Confirmatory evidence was obtained on this point by making filaments of titanium powder and observing their melting points in lamps.

The specific gravity of the metallic beads forged and unforged, varied from 4.46 to 4.53. A mean of four determinations gave 4.50. The specific heat of the metal was found to be as follows:

Temp.	Sp. Heat
0 - 100°	0.1462
0 - 187°.5	0.1503
0 - 254°	0.1516
0 - 333°	0.1563

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[1] Am. J. Sci. 27. 393 (1909).

This method is an admirable one for the preparation of pure titanium. The solid material may be obtained in considerable quantity in a single operation, and of a purity which has not heretofore been reached. The melting point of the pure metal is not as high as the work of other experimenters on impure materials would lead us to believe.

REDUCTION OF CARBON TETRACHLORIDE

The success which attended the reduction of titanium tetrachloride suggested the application of this method to the reduction of the tetrachloride of carbon.

THEORETICAL CONSIDERATIONS

Before proceeding to the experimental part of the work, I performed a simple calculation in so far as the available data allowed on the heat evolved by the reaction and the pressure which it was possible to produce.

If we consider the reaction

$$C\,Cl_4 + 4Na = 4Na\,Cl + C.,$$

we find that the heat of formation of $C\,Cl_4$ is 21,000 calories, and the heat of formation of 4Na Cl is 391,000 calories. The heat evolved by the reaction is therefore 370,000 calories.

Now, if the reaction is complete, this amount of heat is available for raising the temperature of the products of the reaction, viz., Na Cl and C. On the assumption that the heat capacity of 4 Na Cl is 50 calories per degree, and of C is 6 calories per degree, the final temperature of the reaction would be $\frac{370,000}{56}$ or 6,600° C.

The heat capacity of 4 Na Cl however, rises as the temperature increases. If we assume that its heat capacity at high temperatures is double that at ordinary temperatures, the temperature produced by the reaction would be $\frac{370,000}{106}$ or 3490° C., a temperature which is considerable in amount. There is a further assumption involved in this calculation, viz., that the reaction is instantaneous and that no heat passes to the walls of the restraining bomb. A correction for heat lost thereby is not possible. We are assured however, of this one fact; that the temperature attained by the reduction of carbon tetrachloride by sodium must be a considerable one.

It is interesting also to calculate the pressure produced by the reaction.

The critical pressure of carbon tetrachloride at its critical temperature 285° C. is 45 atmospheres. If we consider the vapor of the tetrachloride to act above this temperature as a perfect gas, the final pressure reached at 2500° absolute, would be 364 atmospheres. But, immediately the reaction takes place, the pressure is reduced for that portion of the material to zero. The greatest pressure will maintain when the reaction is half completed. If we consider that the heat from the reduction of one half the material is transferred instantaneously to the other half, the instantaneous pressure when the reaction is half complete would be 182 atmospheres. Now, while no reliance can be placed on this figure for the internal pressure, it is sufficient again to indicate that the reaction must proceed momentarily under a very great pressure indeed. This fact is borne out by the experimental evidence.

EXPERIMENTAL WORK

The first experiments were carried out in the small bomb. Seventy grams of pure C Cl_4 were placed in the bomb and a rod of sodium weighing forty-two grams was enclosed with it. The bomb was then closed and heated by a blast lamp for fifteen minutes. The reduction began below a red heat, and proceeded with explosive violence. The lid of the bomb was raised and the contents emerging at high temperature and pressure melted a channel in the bearing surfaces between the lid and the lower cylinder. The copper gasket at this point had entirely disappeared. A little distance from the point of emission of the charge, the copper gasket was found, melted in with the iron of the bomb. A small amount of a black carbon deposit was all that remained of the charge in the bomb. The experiment was repeated four times and in spite of all precautions, the results were equally disastrous to the bomb.

The larger bomb which had a capacity ten times that of the smaller one, was then taken. In this bomb the six braces distribute the retaining pressure more evenly on the gasket, and serve to retain the lid in place against the lifting pressure of the explosion. The confidence which was placed on the large bomb has been entirely justified in practice, since no explosion has ever taken place in any experiment in which it was used. In the first experiment 200 grams of $C\,Cl_2$ were reduced by 140 grams of Na. The bomb was heated by two blast lamps for half an hour. To indicate the completion of the reaction, a drop of oil was placed on the upper surface of the lid. When the reaction took place the contents of the bomb were projected against the lid, and raised its temperature suddenly, when the drop of oil began to smoke violently, and the heat was turned off. The outside of the bomb was then at a dull red heat. On cooling and opening the bomb, traces only of free sodium were found. The upper portion of the charge contained a considerable quantity of black amorphous carbon in the shape of hollow shells, showing graphitic spots in places. The lower portion contained the fused mass of sodium chloride with which was incorporated the greater quantity of the carbon liberated. The charge was leached out by water and the sodium chloride was removed by washing repeatedly in water. The carbon was then heated with boiling H Cl to remove traces of iron, and dried by washing in alcohol and ether, and set aside for further experiment.

In a second experiment 400 grams of $C\,Cl_4$ was reduced by 240 grams of Na. The reaction was apparently complete at the end of twenty minutes. On opening the bomb, much free sodium was found on top of the charge, due perhaps, to the fact that the Na had been squeezed too tightly in the top of the bomb, and had not melted down before the reaction began. The reduction was thus brought about with too little Na for complete reduction. A considerable amount of ferric chloride was found mixed with the carbon and sodium chloride in the bottom of the bomb. The residue after washing in water was treated with alcohol and ether. The ether residue on evaporation gave indications of a white residue. The whole of the carbon residue was therefore taken and heated to 300° in a current of hydrogen. The solid distillate which was carried over was collected and found to be $C_6 Cl_6$ (melting point 226°). From the point of view of the production of carbon, the result was unsuccessful, but it gave an interesting side light on the production of perchlorbenzene.

In the third and subsequent experiments 350 grams of $C Cl_4$ were reduced in the bomb and gave in all cases, satisfactory reductions. The internal heat produced by each reaction must be considerable. The under side of the lid of the bomb shows evidence of having been superficially melted, some of the solidified metals hanging in drops from its surface. The walls of the bomb were so eaten away as to render its further use unsatisfactory. In some cases large holes were eaten out of the sides and small ingots of metal weighing from thirty to fifty grams were found on the inside of the bomb. The fact that this melting had taken place locally in spots and that the outside of the bomb had never been at a temperature much above 500° C. is an indication that the heat of reaction is a great one. In all cases a single bomb could not be used for more than two experiments and was often rendered useless by the first one. On dissolving the products of these latter reactions in water, it was found that a gas was liberated on solution which burned with a yellow flame quite distinct from that of hydrogen evolved by free sodium in the charge. Ten grams of the charge were therefore taken and dissolved in water. This amount yielded 61.5 ccs. of gas at temperature 25° C. and pressure 760 mm. On shaking 41.2 ccs of this gas with ammoniacal cuprous chloride, 1.5 ccs remained. The gas therefore contained 96.5 ccs of acetylene. This indicates the presence of 1.93% of sodium carbide produced by the reaction.

The carbon produced by the reaction was washed in water, treated with boiling H Cl, again washed with water, with alcohol, and with ether, and finally heated in a current of hydrogen. Analyses of various runs were made by burning the carbon in a current of CO_2-free oxygen and absorbing the CO_2 produced in $Ba(OH)_2$. No hydrogen determinations were made so that the residual percentages in the analyses given may probably represent hydrogen only.

	% Carbon	% Residue
1.	82.8	2.00
2.	85.7	2.30
3.	84.8	3.40
4.	82.2	1.72
5.	85.8	4.71

The specific gravity of the carbon from one experiment was determined by the pyknometric method in benzene and was found to be 1.759.

The carbon from one experiment contained more graphite than was usual. (This was levigated in water and the heavier portion was found to have a specific gravity of 1,905.)

The material is however for the most part amorphous carbon and contains only a small quantity of raphite.

CRYSTALLINE RESIDUE FROM REDUCTION OF $C\,Cl_4$

Since the carbon in the above reductions was liberated from carbon tetrachloride at a high temperature and under considerable pressure, it became a matter of sufficient importance to find out whether there were any signs of fusion in the product produced. Some rounded grains of graphite about the size of small peas were frequently found in the residues after treating with water and hydrochloric acid. It was thought at first that this gave evidence of the melting of graphite, especially so, since the specimens were perfectly rounded in form. The existence of a small amount of iron in this material may lead to the conclusion that the rounded form was given by the incorporation with a large amount of graphite, of a small amount of iron, which was later removed for the most part by solution in hydrochloric acid.

Of much more interest however, than this, are the results obtained by studying the residues which remain after the carbon and graphite have been entirely removed. The method adopted for the removal of these was that followed by Moissan in his attempts on the artificial preparation of the diamond. About 5 grams of the carbon residue were treated with concentrated $H\,N\,O_3$, to which was added from time to time, a few crystals of

$KClO_3$; the mixture being continually maintained on a hot plate at about 100° C. At the end of about three days, the solution cleared and a small white precipitate remained as a residue in the vessel. The graphitic oxide was removed by washing and decantation, and a very small final residue was obtained in the beaker. This residue was transferred to a platinum dish and treated with 50% HF and with boiling H_2SO_4 alternately, then boiled in aqua regia and again treated with HF and with boiling H_2SO_4. Finally after about six of these successive treatments, the residue, which was but infinitesimal in amount was transferred to a watch glass and observed under the microscope. The residue consisted of a considerable number of fine crystalline grains, for the most part colorless and transparent, but some showed a pale yellow or a pale blue color. No definite crystalline structure was visible in any of them. Under crossed Nicols they showed a small amount of double refraction. These are quite distinct from glass and silica, small particles of which are always in evidence in any solution which comes in contact with a laboratory atmosphere. These crystals appeared again and again on successive treatments with HF and H_2SO_4, being quite insoluble in these reagents. On placing them in a solution of methylene iodide in a small test tube, they were recovered from the bottom of the solution. Their specific gravity is therefore greater than 3.3. The largest crystals which has been observed, showed a greatest length of 0.352 m m. and a greatest breadth of 0.192 mm. In no case was any definite shape observed. The crystals appeared always as irregular fragments. There was no evidence of fusion in any of the crystalline grains. The residues were too small in amount to make any attempt at determining their nature by combustion, but from the nature of origin and from the fact that they so effectively resist attempts to dissolve them, I am led to suppose that this residue is nothing but a form of crystalline carbon.

REDUCTION OF CARBON DISULPHIDE BY SODIUM

While considering the reduction of carbon from its tetrachloride it seemed of interest also to attempt the reduction from liquid carbon disulphide by the same means.

It is well known that carbon disulphide is an endothermic substance yielding up 26,000 calories by its decomposition from the gaseous state. From considerations similar to those detailed in the case of carbon tetrachloride the temperature attained by its reduction with sodium is between 2,500° C. and 4,500° C. From similar considerations with regard to its critical temperature and pressure the maximum pressure attained when the reaction is half complete is in the neighbourhood of 300 atmospheres. In one experiment 206 grams of carbon disulphide were reduced by 250 grams of sodium. The theoretical yield of carbon should be 32.5 grams. A total amount of 24.9 grams was obtained in various states of division, this being a percentage yield of 76.6%. In a second experiment in which 187 grams of carbon bisulphide were taken, 22.4 grams of carbon were obtained, the percentage yield being 77.7%.

The reaction is much more severe on the metal of the bomb than the reduction of the tetrachloride. After each experiment a new bomb had to be prepared. Much sodium carbide was produced by the reaction and very little free sodium was found. The carbon is again almost entirely in the form of amorphous carbon. On removing this carbon by nitric acid and potassium chlorate, and treating the residue with HF and boiling H_2SO_4 small crystalline residues were obtained, similar to those produced by the tetrachloride, but the amount of this residue was again infinitesimal. No further information was gained from these results as to the conditions for the formation of crystalline carbon at the moment of its liberation from its compounds.

REDUCTION OF BERYLLIUM CHLORIDE

A sample of basic beryllium carbonate sent to me by Prof. Chas. James, of Durham, N. H., served as a starting point in the preparation of beryllium chloride. This material was converted into oxide mixed with lamp black by means of a sugar solution, and heated in a current of hydrogen, and finally chlorinated in small portions in hard glass tubes. The beryllium chloride which sublimed over was continually resublimed in a current of chlorine till the greater portion of the green chlorides of iron were removed.

The final product showed only a pale pink coloration when solidified after melting. The sublimed crystals before melting were pure white. The successive portions of the chloride thus produced were rapidly transferred to a well stoppered bottle and preserved.

In the first attempt at reduction of the chloride 38 grams were taken and mixed with 21.8 grams of sodium in the small bomb. The reaction proceeded well. Very little free sodium was found. Some small beads were found at the bottom of the bomb in appearance like metallic silver. These were soft and easily flattened. The finely divided material after elimination of sodium by alcohol was thrown into water and produced a rapid effervescence of hydrogen. On the conclusion of the effervescence, the wash water contained a considerable quantity of a grayish black flocculent material which may be some form of beryllium hydrate. The rest of the chloride (88 grams) was then reduced in the large bomb with an excess of sodium (60 grams). The sodium was removed by absolute alcohol and the sodium chloride by water. A considerable quantity of small metallic beads were recovered from the residue and the remainder was in the form of fine metallic dust through which small rounded particles of metal were to be seen. The total yield of metal was however, only 26.3 %. A considerable quantity of the Be material is transformed into the grayish black flocculent precipitate mentioned above.

The solid beads are undoubtedly metallic beryllium. Their specific gravity was found to be 1.793. They dissolve readily in dilute sulphuric acid. Ammonium carbonate throws down a white precipitate from this solution which is soluble in excess. The precipitate reappears in a flocculent form on boiling. Ammonia precipitates from the solution a white gelatinous hydrate. A test for iron with NH_4CNS in HCl solution yielded only a faint coloration. No ultimate analysis of this material has yet been made. There is no doubt that when the experiment is carried out in a still larger scale that a quantity of metallic beryllium may be easily made.

REDUCTION OF SILICON TETRACHLORIDE

The silicon tetrachloride used was prepared by chlorinating the impure silicon obtained by reduction in the electric furnace.

The chlorides of the heavier metals which pass over the $SiCl_4$ were easily removed by successive fractional distillation. That portion of the liquid chlorides which boiled between 57°.5 C. and 58° C. was collected and given a final treatment by shaking with mercury and with sodium amalgam. The liquid chloride which was then distilled had a constant boiling point of 57°.7 C. The reduction of this silicon tetrachloride was attended with considerable difficulty. When the liquid chloride was poured into the bomb, the vapor of the chloride which contains finely divided silicic acid in suspension invariably settled in the gasket and prevented the formation of an air tight joint. This could not be entirely eliminated either by cooling the bomb before the material was introduced or by subjecting the gasket to an abnormal pressure. The consequence of this was that the silicon chloride, which it was intended to reduce, leaked out of the bomb in the first few minutes of the heat. In the fourth attempt the bomb was filled with silicon chloride and the requisite amount of sodium for its reduction. The gasket was then put in position and the lid was pressed down upon it by a hydraulic pressure of 100,000 lbs. The yoke was then screwed on the bomb without disturbing the lid. In spite of this precaution, the pungent odor of silicon chloride was detected during the heat. Some of the material however stayed in the bomb and was reduced. The reduction was apparently incomplete since much free sodium was found in the bomb.

The product of the reaction was thrown into alcohol to remove the free sodium. The finely divided silicon in the mass reacted with the alcohol, yielding a white gelatinous mass surrounding the larger black particles of reduced silicon. This material when thrown into water ignited with a succession of violent explosions resembling the burning of $Si\ H_4$. These explosions were prevented by dissolving the material in a strong solution of hydrochloric acid. In dilute hydrochloric acid, the black residue passed over gradually into a white gelatinous precipitate probably $Si\ O_2$ in a hydrated form. Some metallic beads were picked out of the final residue. These were hard and brittle and were thought to be metallic Si. They were however easily soluble in hydrofluoric acid, contained much iron, and had a specific gravity of 5.44. This indicates their composition to be $FeSi_2$. The finely divided material which was saved by rapid washing in water also contained much iron from the sides of the bomb.

It will be seen therefore that the reduction of silicon tetrachloride is too difficult to be of any practical value. The reaction is further incomplete and the small amount of material which was obtained was largely contaminated with iron picked up from the sides of the iron bomb.

REDUCTION OF NEODYMIUM CHLORIDE BY SODIUM

During the progress of the work the possibilities of this method as means of reducing the metals of the rare earths was suggested to me.[1]

Some neodymium chloride was accordingly prepared and its reduction attempted by sodium. Ninety-four grams of the chloride were taken, and mixed with 26.5 grams of sodium and heated in the small bomb. On cooling and opening the bomb, the free sodium was removed by solution in alcohol. The residue consisted of sodium chloride and finely divided metallic neodymium. There was no trace of any fusion of the metal. On attempting to dissolve out the sodium chloride in water, the neodymium metal was itself immediately attacked by the water so that a separation became impossible.

A further attempt to melt the metal in an alumina crucible in the Arsem vacuum furnace failed because the metal slagged immediately with the crucible.

In a magnesia crucible under the same conditions, the metal was converted into a carbide before the sodium chloride was entirely melted. Further reductions were tried and all with the same result. It does not seem possible by this means to obtain Nd metal in the molten condition. The finely divided powder which is obtained is difficult to melt without introducing some contamination.

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[1] I am indebted to Prof. Chas. James for this suggestion as well as for the materials on which to work.

CONCLUSIONS

The results of the preceeding experiments may be briefly stated as follows:—

1. Titanium tetrachloride may be readily reduced by sodium in a closed bomb. If the amount of material used be sufficiently great, the heat of the reaction is sufficient to give the titanium metal in a coherent metallic condition.

2. Carbon tetrachloride and carbon disulphide may be reduced by sodium. The temperature and pressure produced by the reaction is considerable. There is no conclusive evidence of the fusion of any part of the material during the reduction. A crystalline residue, microscopic in amount appears to possess some of the properties of crystalline carbon.

3. By the reduction of the tetrachloride and disulphide of carbon with sodium, some sodium carbide is produced as a by-product of the reaction. With too little sodium to complete the reduction of the tetrachloride some carbon hexachloride is produced.

4. Beryllium chloride may be readily reduced by sodium and obtained in the metallic condition. Its properties will be further investigated.

5. Silicon tetrachloride may be reduced only with difficulty by sodium. Considerable trouble was experienced in maintaining an air tight bomb. The metal obtained was in a finely divided condition.

6. Neodymium chloride is reduced by sodium. The metal was found in a finely divided condition and could not be readily separated from the sodium chloride produced by the reaction.

ON NATURAL AND ARTIFICIAL SULPHOANTIMONITES AND SULPHOARSENITES

By Prof. Dr. F. M. Jaeger, Groningen (Holland)

(*Inorgan. Chemical Laboratory of the University*).

Section 1. I wish to give here the record of a series of investigations executed in my laboratory during the last year by myself and by my present assistant, *Dr. H. S. van Klooster*. As our purpose was to see, which natural sulphoantimonites and sulphoarsenites could be obtained from binary molten magmas, we first needed to know, in how far the pure components, which we used could crystallize from such liquids. As for a number of these components such data were already obtained by other investigators, it was finally only necessary to study the mutual behavior of the elements: sulphur and silver, and sulphur and antimony with respect to each other.[1] Some of the data about the sulphosalts were already published in a short preliminary paper in the Kon. Akad. van Wetensch. Amsterdam, (1 and 2), but have not yet appeared in another language than the Dutch elsewhere; a number of data given here are, however, quite new. The paper treats therefore of the phenomena occurring in the binary systems of: *Sulphur* and *Antimony, Sulphur* and *Silver, Silversulphide* and *Antimonysulphide, Leadsulphide* and *Antimonysulphide, Silversulphide* and *Arsenicsulphide,* and *Pyrargyrite* and *Proustite.*

Sulphur and Antimony

Section 2. Although the mutual behavior of sulphur and antimony has been already a subject of investigation more than once, only a short time ago the complete diagram was given of the melting phenomena with binary mixtures under atmospheric pressure, by *Pélabon* [Ann. de Chim. et Phys. (8) *17*.526. (1909); Compt. rend. *138*.277:*140*.1389]. However, the explanation of the observed phenomena is at least very peculiar and in many respects wholly wrong. In connection with a study of the natural sulphoantimonites, and with a further research as to the remarkable photoelectric effect, discovered by *Jaeger* in 1907 [*F. M. Jaeger*, Kon. Akad. v. Wet. Amsterdam, Proceed. (1907) 810; Z. f. Kryst. *44*.45. (1908)], a better knowledge of the possible compounds in this system was most desirable. For the same reason, we have undertaken the investigation of the mixtures of silver and sulphur.

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[1] *F. M. Jaeger*, Verslagen Kon. Akad.van Wet. Amsterdam (1911). 497.

[2] *F. M. Jaeger* and *H. S. van Klooster*, Verslagen Kon. Akad. van Wet. Amsterdam (1911) 510.

The method used is the same we followed in the study of the system tellurium and sulphur [*Jaeger*, Versl. Kon. Akad. v. Wet. (1910). 606].

To prevent oxydation, all determinations were made in an atmosphere of nitrogen; the total amount of materials used in these experiments was always 20 grams.

BINARY MELTINGPOINTLINE OF ANTIMONY AND SULPHUR

Compositions of the mixtures in at.proc.S.	in weight proc.S.	1st. Eff.	Time in seconds	2nd Heat Eff.	Time in seconds
0	0	632°	—	—	—
2.5	0.68	628	—	—	—
4	1.09	620	—	—	—
5.4	1.38	618	360	499°	—
10	2.87	614	340	500	40″
15	4.49	616	370	499	40
20	6.25	616	360	501	80
30	10.25	614	260	509	90
40	15.10	614	280	516	100
50	21.06	610	260	520	140
55.4	24.8	612	240	520	180
59	27.74	537	——	523	80
60	28.58	546	——	——	—
61.-63.8	——	543-530	100-60	110	—

SECTION 3. Figure 1 gives these data in graphical representation. From this it is clear that both elements, if melted together, give only a single compound, i.e. Sb_2S_4, which melts at 546° C. At this temperature already a slight dissociation can be observed,

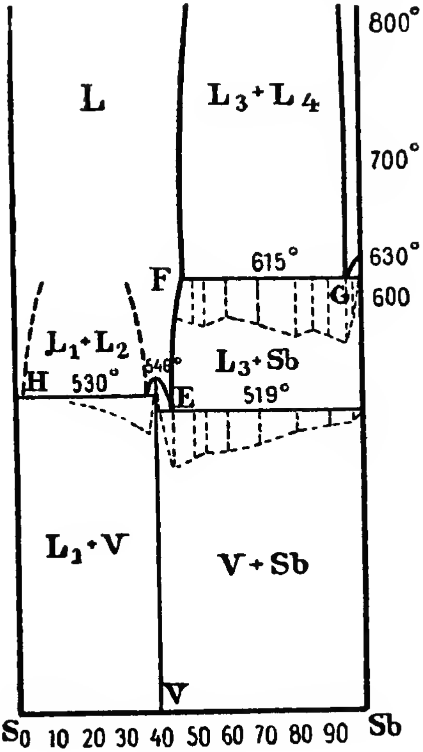

Fig.1

as *Guinchant* and *Chrétien* (Compt. Rend. *142*.709; *139*.288; *138*. 1269) have mentioned. There are two eutectic temperatures at both sides: at. 61,3% sulphur and 530° C, and at 55 at. proc. sulphur and 519° C.

If the concentrations of sulphur are lower or higher, there is a system of two liquid layers possible. For the transformation temperature of the one system of two liquids, the temperature

615° C. was found; the caloric effects are very great, and the coexisting liquids at 615° C. contain 5%, resp. 45% sulphur.

It is very difficult to obtain the compound Sb_2S_3 in a pure state; the product always contains too much or too little sulphur, so that the meltingpoint is in each case lowered. For a short time *J. Olie* and *H. R. Kruyt*, who studied the photo-electric phenomena of antimonysulphide again, stated by electrical resistance measurements, the existence of a very small mixed crystal-series, to about 0.3 at. proc. starting from Sb_2S_3 to the *Sb*-side. [Proceed. Kon. Akad. v. Wet. Amsterdam (1912). 740]. We found that a small amount of sulphur can be extracted with hot toluenc. It is not yet clear in what manner these properties are related to the photo-sensitiveness of the compound.

Guinchant and *Chrétien* (loco cit.) have calculated the cryoscopic constant of Sb_2S_4 at 791° C, if *Sb* is the solved substance; from the observed depressions of Ag_2S or $Pb S$ are added, 791°,1 follows; from *Pélabon's* experiments with $Hg S$ and Cu_2S, 792°,5. We must suppose that Sb_2S_3 is in that case not considerably dissociated. The heat of fusion is calculated from these data at 17.2 Cal. pro gramm, while the direct determination gave 17.5 Cal. pro gramm. The true specific heat at 500° C. is 0.220, while the liquid at 582° C. has a specific heat of 0.263.

If more sulphur to $Sb_2 S_3$, is added than 60 at. proc., the solidifying-temperature is lowered. At 61% *S* it is 541° C, but already at 61.3% *S* the liquid is split in two layers, with a transformation temperature of 530° C. Even at 80% and 70% *S* this temperature could be observed again; but at 90% *S* the vaporization of the sulphur was a greatly disturbing fact. We found only one eutectic temperature, at 110° C — thus quite in the vicinity of the true meltingpoint of sulphur. There was no indication found of a compound $Sb_2 S_5$; it seems not to be obtainable in this way.

SULPHUR AND SILVER

SECTION 4. The mixtures of silver and silversulphide have been studied also more than once, but with divergent results. *Pélabon* (loco cit.) mentions a rectilinear depression of the meltingpoint of pure silver (960°) to 800° C, and 31% *S*; he is of opinion that this point is the first eutectic point, and that the meltingpoint curve then rises immediately to the meltingpoint of Ag_2S. Mixtures containing more sulphur could not be investigated by the vaporization of the sulphur. These results are however contrary to those of *Friedrich* and *Leroux* [Metallurgie, *3*.361 (1906); *4*. 485 (1907)]. They give the meltingpoint of 99.6% Ag_2S at 835° C, which temperature would be increased by more sulphur, which for instance is known to be the case with FeS. All the investigators conclude to a partial miscibility in the liquid state. *Friedrich* and *Leroux's* data agree principally with mine; however their conclusions differ in some points from mine, which can be explained partially by the fact, that they worked in an oxygen-atmosphere, and the silver solves oxygen to a certain amount. Another consequence of their method is the oxydation of Ag_2S, with the formation of SO_2, so that it is impossible to give a good value for the meltingpoint of Ag_2S. Therefore we made all the experiments in an atmosphere of pure nitrogen. Some doubt has been expressed as to the real transformation of two liquid layers and one solid phase at the corresponding temperature. For if no forming of mixed crystals is supposed to be possible, the end of it must be the presence of two solid layers, one of them being pure Ag, the other Ag_2S. However in the lower layer, there was found as much as 16% S; a quantity too large to be explained by accidental convection only during the transformation of the two liquid layers. Although we were really able, by observing the time of transformation at 906° C, to prove that a real two-layer-equilibrium was present here, we found an inhomogeneous structure of the two layers, notwithstanding that we made these experiments in a nitrogen-atmosphere. This was proved by means of several analyses made of the layers in different places; thus an influence of some diffusion-phenomena must be supposed in all these cases.

SECTION 5. The experiments were made in porcelain test-tubes; graphite-tubes were rejected, and in the same way we protected the thermo-element by means of porcelain tubes, instead of nickel tubes, as the German investigators have done.

Pélabon determined the meltingpoint of Ag_2S at 825° C; *Friedrich* and *Leroux* do not give this temperature at all, because they could not come to higher concentrations than 97 weight proc. of

Ag_2S, because of the particular circumstances of their experiments. The temperature mentioned by *Pélabon* certainly is too low; in former papers he gives the values: 840° C. and 845° C. (Compt. Rend. *136*. 1450, and *137*. 920). The reason of this is, that Ag_2S at 950° C. dissociates already in a perceptible way. Working in a slowly moving nitrogen-current, the sulphur is found just above the liquid, otherwise in the upper part of the tube. If however one works in air, the Ag_2S_2 is oxydised, and SO_2 is evolved. As the meltingpoint of Ag_2S is rapidly lowered by traces of admixed silver, the discrepancies in the respective data are clearly explained. Indeed, if the heating-up of the substance is not executed with great care and to no higher temperature than only a little above 845° C. we find not only another meltingpoint at successive determinations, but at the same time the effect at 806° C. lasts longer and longer; as the true value for a very pure, analyzed preparation, heated only just above its meltingpoint, we found 842° C. — which value is in perfect agreement with the values given by *Pélabon*.

The opinion that *Ag* and Ag_2S could be melted together in all proportions, to form so-called "niello," is shown to be wrong. As soon, as more than 10% *S* is present, the two liquid layers appear, and with increasing amount of sulphur, their masses vary by the growing of the upper layer. After solidification, it is easy to see both layers; the sharp boundary line between them indicates, that liquid Ag_2S does adhere to the wall of the porcelain tube, liquid *Ag* however does not.

Another question is the possibility of solid solutions between *Ag* and Ag_2S: *Friedrich* and *Leroux* do not confirm this. When the concentrations are lower than 4 or 5 at. proc. *S*., the eutectic temperature could be no longer observed. For the depressions of the meltingpoint of pure silver by Ag_2S, we found:

For 2 at. proc. *S* : 13°
For 5 at. proc. *S* : 44°.

As the heat of fusion is 21.1 to 24.7 Cal., the cryoscopic constant for molten *Ag* must be about 1324° C. If no formation of mixed crystals occured, the depression in these cases must have been 26° and 67° respectively, if Ag_2S was the solved substance. The observed values therefore are much too small; a fact that points to real formation of solid solutions, if we could be sure that no very complex molecules $(Ag_2 S)$n were to be formed. In every case the concentration of these mixed crystals cannot increase to a considerable amount, as *Friedrich* and *Leroux* have already pointed out.

The eutectic mixture E lies at 94.8 weight proc. $Ag_2 S$; thus the meltingpoint of $Ag_2 S$ is lowered by only 5% Sulphur already 36° C. All mixtures containing $Ag_2 S$ have an inversion temperature at 179° C; the maximal transformation-time occurs with the pure compound. Perhaps the $Ag_2 S$ shows some other peculiarities at lower temperatures, but we are not yet quite sure of it.

If the amount of sulphur surpasses 33.3 at. proc. then the S vaporizes at 800° C. already with too great rapidity to make investigation again possible.

The obtained data are given below; they are represented graphically in Fig. 2, which does not need further explanation.

BINARY MELTINGPOINT CURVE OF SILVER AND SULPHUR

Composition of the mixtures in		1st Heat Effect	Time in seconds:	2nd Heat Effect	Time in seconds	3d Heat Effect	Time in seconds
Atom proc. S.	Weight proc. S.						
0	0	961°	—	—	—	—	—
2	0.61	948	—	—	—	180	—
5	1.54	917	—	806	—	179	20″
10	3.20	905	115	805	10	179	30
20	6.9	906	65	804	40	179	60
30	11.1	900	15	806	50	179	100
32	12.1	—	—	806	60	179	130
33⅓	12.9	842	—	—	—	179	145

We have not reproduced photographs of etched surfaces, because they are comparatively simple. The silversuplhide separates as a primary crystallisation in small cubic crystals; the antimony sulphide shows long-shaped flat needles. We shall have an opportunity to return to them again, when we shall investigate the silversulphoantimonites. The inversion temperature of 179° C with the Ag_2S is probably the transformation of the cubic form (argyrite) more stable at higher temperatures, to the form of rhombic symmetry more stable at lower temperatures, occurring in nature perhaps as acanthite.

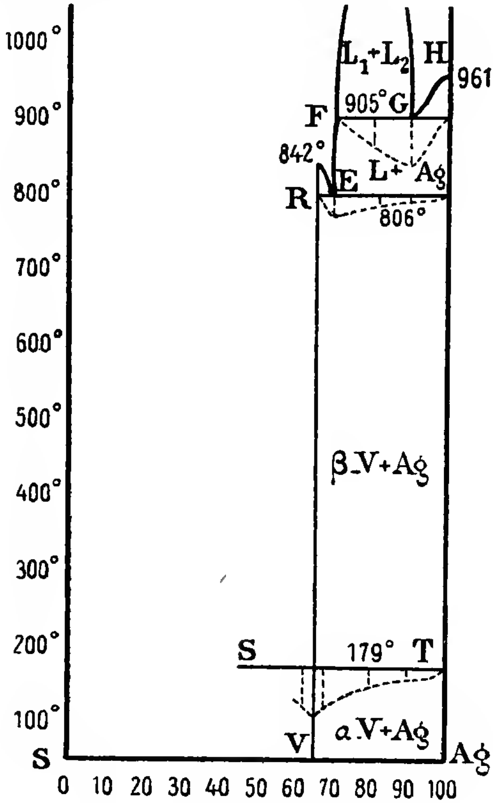

Fig. 2.

SILVERSULPHIDE AND ANTIMONYSULPHIDE

SECTION 6. Under the natural sulphoantimonites an important class is formed by those, which contain silver and antimony; a summary is given below. The compounds Sb_2S_3 and Ag_2S also occur in nature; the first one as a rhombic *antimonite*, the second one as regularly crystallizing *argyrite*, and perhaps in a rhombic form as *acanthite*; as we have seen in the former investigations, they are really the only compounds to be met with in melting together silver and sulphur, resp. antimony and sulphur, while the diagram showed an inversion temperature of 179° C. with $Ag_2 S$. The natural sulphoantimonites are the following:

$Sb_2 S_3 + 0.16$	$Ag_2 S$	bolivianite	not well determined
$Sb_2 S_3 + 5$	$Ag_2 S$	stephanite	rhombic
$Sb_2 S_3 +$	$Ag_2 S$	miargyrite	monocline
$Sb_2 S_3 +$	$3\ Ag_2 S$	pyrostilpnite	monocline
$Sb_2 S_3 +$	$9\ Ag_2 S$	polybasite	monocline
$Sb_2 S_3 +$	$3\ Ag_2 S$	pyrargyrite	ditrigonal-pyramidal
$Sb_2 S_3 +$	$12\ Ag_2 S$	polyargyrite	cubic.

Of these compounds, miargyrite is a derivative of the metasulphoantimonous acid: $H\ Sb\ S_2$, while pyrargyrite and pyrostilpnite are derivatives of the corresponding ortho-acid: $H_3Sb\ S_3$; derivatives of the pyro-acid: $H_2\ Sb_2\ S_5$ are unknown in nature.

SECTION 7. Often trials have been made to prepare these sulphoantimonites: *De Sénarmont* obtained pyrargyrite from the amorphous product by heating it with solutions of $Na\ H\ CO_3$, in sealed tubes at 100° - 300° C. [Ann. de Chim. et Phys. (3). *30.* 129,146 (1850); *22.* 129,175 (1851)]. *Doelter* pretends to have prepared from a mixture of $Ag\ Cl$, $K_2\ H_2\ Sb_2\ O_7$, $Na_2\ CO_3$ and $H_2\ S$ — solutions once miargyrite, and further stephanite and pyrargyrite, but more detailed data are absent.

We found pyrargyrite as a result of Na_2 S — solutions with $Ag_2\ S$ and $Sb\ Cl_3$, the greater part of the $Sb_2 S_3$ formed remained in the Na_2S solution, even after heating at 200° C. during 50 hours. If, however, we added $Na\ H\ CO_3$ to the sulphide for about equal weights, we obtained all the antimony in the form of pyrargyrite. The presence of $Na\ H\ CO_3$ or Na_2CO_3 seems in all cases to be very favorable. Heating to 100° C. had not much effect, but a temperature of 200° C. is sufficient, if sustained about 48 hours. We intend to study these reactions more systematically.

H. Sommerlad [Zeits. f. anorg. Chem. *15* .173 (1895); *19.* 420 (1898)] thinks, that he has obtained miargyrite, stephanite, and polyargyrite by melting together $Sb_2 S_3$ with $Ag\,Cl$, after eliminating the $Sb\,Cl_3$ formed by distillation. However, *F. Ducatte* (Thèse, Univ. Paris, 1902) and *J. Rondet* (Thèse, Univ. Paris 1905) showed that this is certainly not true, because there are always formed in this case halogenated compounds. Their very complicated " compounds " however are neither homogeneous substances, but mixtures; the composition varies with the quantities of the components used.

As we shall see below, of all these minerals only *two* are to be obtained from binary molten mixtures, i. e., *miargyrite*: $Ag\,Sb\,S_2$ and *pyrargyrite*: $Ag_3\,Sb\,S_3$. Stephanite lies in the immediate vicinity of an eutectic mixture. As the symmetry of the crystal-form is different from each of the components, it must be assumed that from this eutectic mixture there can be formed a real compound at a much lower temperature, if solvents are present. The other minerals are in no evident relation to the meltingpoint diagram; they cannot be formed from binary molten mixtures. To the same conclusion we must come in the case of the other systems of sulphides, as we shall see. Therefore it can be assumed with great probability, that those natural sulphides are not formed from magmas, but certainly by pneumatolytic or sedimentary processes, and from mixtures with volatile solvents.

SECTION 8. Regarding the mentioned binary system, there are some orientating, but very insufficient data of *Pélabon* (Compt. Rand. *136*. 1450.) while *Guinchant* and *Chrétien* published some cryoscopical data about diluted solutions of $Ag_2\,S$ in molten $Sb_2\,S_3$ (Compt. Rend. *138*. 1269). *Pélabon* says, that the binary meltingpoint line consists of six linear parts; but the situation of the eutectic points and the corresponding temperatures are given in a quite insufficient way: for one of the maxima there is no temperature given at all, and of one of the minima, the composition is quite undetermined. Also the composition of the other points is given in a quite insufficient way. The data of *Guinchant* and *Chrétien*, if recalculated in mol. proc., agree very well with the figures we obtained for the corresponding branch of the meltingpoint curve:

For 6.58 mol. proc. $Ag_2\,S$, t = 522° C.
13.5 mol. proc. $Ag_2\,S$, = 505° C.
19.4 mol. proc. $Ag_2\,S$, = 487° C.
26 mol. proc. $Ag_2\,S$, = 462° C.

SECTION 9. The used components were purified from superfluous sulphur by means of toluene, and analyzed. It was very difficult to obtain a product of the constant composition $Sb_2 S_3$. The total mass of all the mixtures was in all cases 20 gramms; they were melted in a nitrogen-atmosphere repeatedly, pulverised and again melted. By the side of pure $Ag_2 S$ the heat-effects are very small, which gives some difficulties in determining these points with great accuracy; however the eutectic temperature can always be accurately observed. Above 800° or 900° C. some splitting-off of sulphur occurs, so that it is of importance to heat rapidly and with great care. The molten mass is thin and and not very viscous; so it can be stirred in a sufficient way.

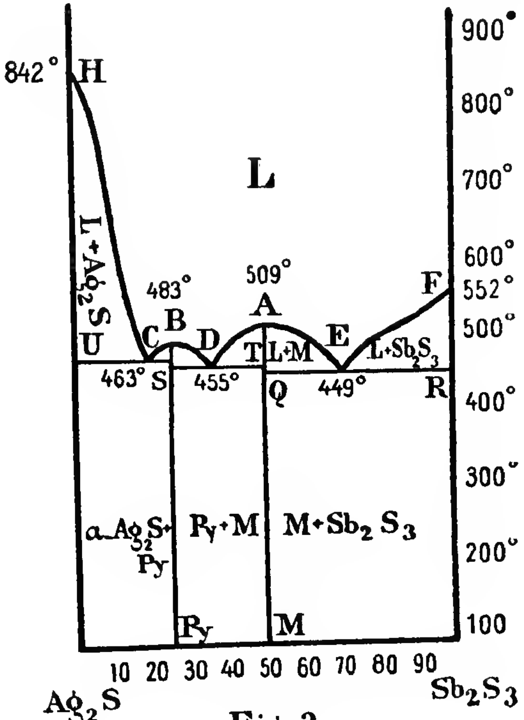

Fig.3.

It seems that the solidified mass shows again an inversion at a lower temperature; however it was not possible with the present means, to find out completely what occurred. Some mixtures give a heat-effect at about 73° C; but the time, during which the temperature remained constant, was not well determinable.

The obtained data are given in the table below; graphically they are reproduced in the Fig. 3. Retardation phenomena were happily seldom, and commonly only feeble.

BINARY MELTINGPOINTLINE OF SILVERSULPHIDE AND ANTIMONYSULPHIDE

Composition of the mixtures in					
Mol. Proc. $Ag_2 S$	Weight Proc. $Ag_2 S$		1st H. Eff.	2nd H. Eff.	Time in seconds
0	0	F	546°	—	—
5	3.73		529	—	—
10	7.56		510	443°	10″
15	11.50		499	450	30
20	15.55		479	447	40
25	19.70		462	453	90
28.2	22.43	E	—	451	120
30	23.98		460	452	85
35	28.39		482	447	30
40	32.92		498	451	10
45	37.59		506	—	—
50	42.41	A	509	—	—
55	47.36		500	453	90
60	52.83		479	454	120
63.5	56.16		469	458	250
64.5	57.23	D	—	458	270
65	57.76		464	455	200
70	63.21		475	454	35
75	68.84	B	483	—	
80	74.65		470	463	380
81	75.98	C	—	464	395
83.34	78.65		466	464	260
85	80.66		505	464	245
90	86.89		595	463	170
92.3	89.82		647	458	100
95	93.33		710	463	70
100	100.	H	842	—	—

There cannot be found an inversion-temperature of the compound $Ag_2 Sb S_3$. That this substance, with its meltingpoint of 486° C. was really *pyrargyrite* could be checked by several methods. The spec. grav. of the compound was determined by means of a pycnometer, with paraffine-oil as the immersion liquid. It was found to be: 5.790 at 18° C; for the natural pyrargyrite were found values, ranging from 5.75 - 5.85, while a pyrostilpnite of *St. Andreasberg* showed a spec. grav. of only 4.2 - 4.3. Natural pyrargyrite was melted; the meltingpoint was found to be 481° C. Further the colour (violet), shape and stripe on porcelaintable, were quite the same as of natural pyrargyrite, so that there cannot be any doubt about the identity of the two substances.

In the same way we determined the spec. grav. of artificial *miargyrite;* pycnometrically we found: 5.36, while the natural miargyrite has a spec. grav. of 5.1 - 5.3. In the same way a comparison of colour, and other properties confirmed the identity of natural and artificial products.

The study of these substances, in comparison with natural pyrostilpnite and miargyrite confirms in many respects the hypothesis, that the natural minerals are formed by sedimentary processes, rather than from molten magmas. The pyrostilpnites of *Przibram* in Boheme, often are situated in quartz, and deposited there in as thin layers, also they have been found with veins of pyrite on calcite; or with pyrargyrite and leadsulphite, in evidently sedimentary products. A miargyrite of *Przibram* showed to be a dense mass in quartz; the whole impression was that of a mineral complex, formed from solutions.

SECTION 10. On the first branch (HC), pure $Ag_2 S$ is eliminated; this branch being almost rectilinear, we tried to calculate the cryoscopic constant of $Ag_2 S$. The observed depressions were:

For 1 mol proc. $Sb_2 S_3$, 37°
For 2 mol. proc. $Sb_2 S_3$, 62°
For 3 mol. proc. $Sb_2 S_3$, 102°.

For 100 gramms of $Ag_2 S$ therefore the molecular cryoscopic constant would have the enormous value of 8108° — in accordance with the very small heat of fusion of $Ag_2 S$, which is about 1/7 or $\frac{1}{8}$ of that of pure silver.

Some of the reguli were polished and then attacked by means of different solutions. The reproductions 4 - 8, show some of the results. In Fig. 4 (Enlargements are all about 25 times), the cubic, dark $Ag_2 S$ is seen as primary crystallisation on the background; in Fig. 5, the $Ag_2 S$ is much less in the midst of a quasi-homogeneous mass, which is the eutectic mixture C; Fig. 6 is pyrargyrite, here and there with hexagonal peripheries. This preparation has all properties of the natural mineral: in thin plates red-transparent, in reflected light a beautiful violet, etc. Fig. 7 regards the eutectic mixture E and shows miargyrite and antimonite in almost the same quantities; the preparation is etched by natriumsulphide. A layer-structure is not observed; a fact, very common in such mixtures, with the exception of these of metals. In fig. 8 the preparation is also attacked by sodium-sulphide; the $Sb_2 S_3$ is seen in characteristic long-straped crystals as a primary crystallisation, in greater quantity.

LEADSULPHIDE AND ANTIMONYSULPHIDE

SECTION 11. In an analogous way the study of the binary mixtures of lead-sulphide and antimonysulphide was begun; also of this class a lot of minerals are met in nature:

Zinckenite	$Pb\,S + Sb_2\,S_3$	rhombic-bipyramidal.
Plagionite	$5\,Pb\,S + 4\,Sb_2\,S_3$	monocline-prismatic.
Warrenite (or Domingite)	$3\,Pb\,S + 2\,Sb_2\,S_3$	rhombic-bypyramidal.
Heteromorphite	$7\,Pb\,S + 4\,Sb_2\,S_3$	monocline-prismatic.
Tamesonite	$2\,Pb\,S + Sb_2\,S_3$	rhombic-bipyramidal.
Semseyite	$9\,Pb\,S + 4\,Sb_2\,S_3$ or $7\,Pb\,S + 3\,Sb_2\,S_3$	monocline-prismatic.
Boulangerite	$5\,Pb\,S + 2\,Sb_2\,S_3$	rhombic-bipyramidal.
Meneghinite	$4\,Pb\,S + Sb_2\,S_3$	rhombic-bipyramidal.
Geocronite	$5\,Pb\,S + Sb_2\,S_3$	rhombic-bipyramidal.
Kilbrickenite	$6\,Pb\,S + Sb_2\,S_3$	

The Epiboulangerite is a sulphoantimoniate: $3\ Pb\ S + Sb_2\ S_5$; from the mentioned minerals the zinckenite is a derivative of the

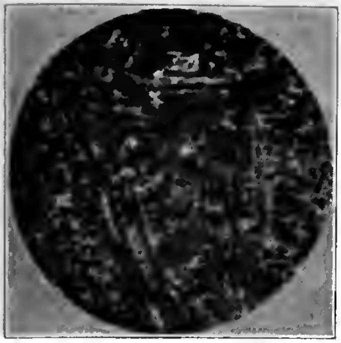

Fig. 4.
95% Ag_2S + 5% Sb_2S_3.
(Strong Hydrochloric Acid.)

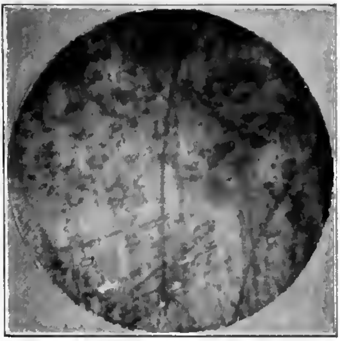

Fig. 5.
83.3% Ag_2S + 16.7 Sb_2S_3.
(Strong Hydrochloric Acid.)

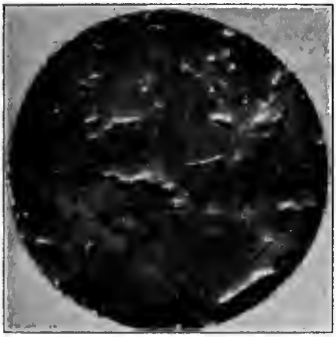

Fig. 6.
75% Ag_2S + 25% Sb_2S_3
(Potassium hydroxide.)

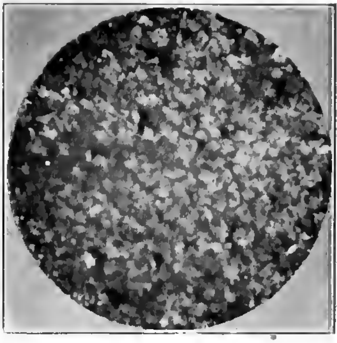

Fig. 7.
28.2% Ag_2S + 71.8 Sb_2S_3.
(Sodium sulphide.)

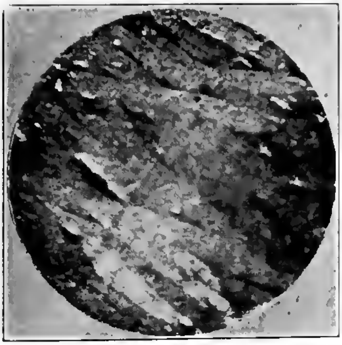

Fig. 8.
5% Ag_2S + 95% Sb_2S_3.
(Sodium sulphide)

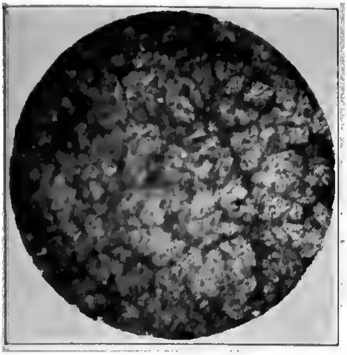

Fig. 10.
90% PbS + 10% Sb_2S_3.
(with strong HCl)

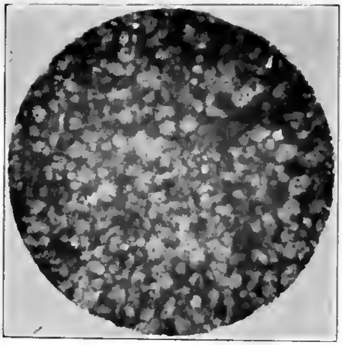

Fig. 11.
80% PbS + 20% Sb_2S_3.

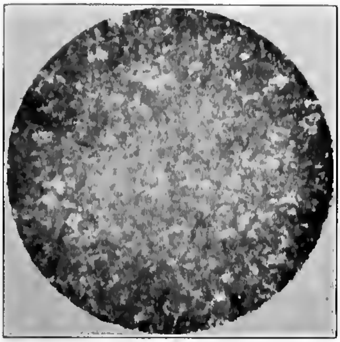

Fig. 12.
66.67% PbS + 33.33% Sb_2S_3.

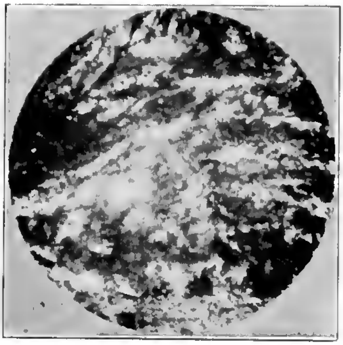

Fig 13.
60% PbS + 40% Sb_2S_3

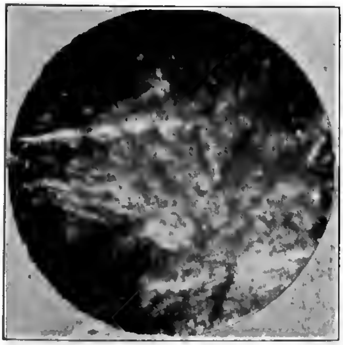

Fig. 14.
57.5% PbS + 42.5% Sb_2S_3.

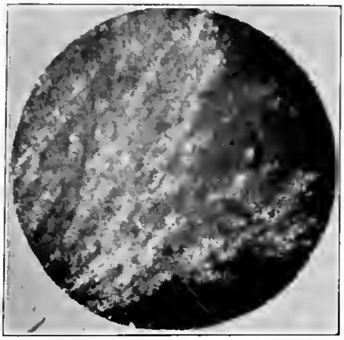

Fig. 15.
55.55% PbS + 44.45% Sb_2S_3.

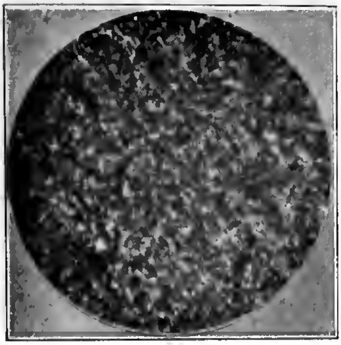

Fig. 16.
50% PbS + 50% Sb_2S_3.
(with Na_2 S.)

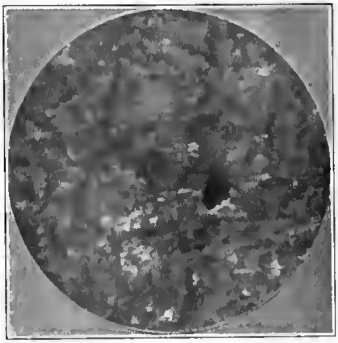

Fig. 17.
40% PbS + 60% Sb_2S_3.

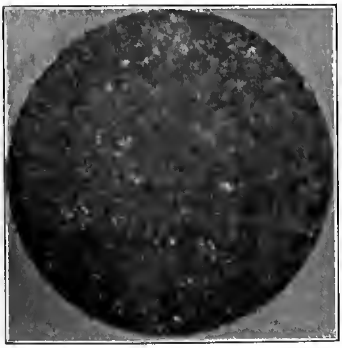

Fig. 18.
20% PbS + 80% Sb_2S_3

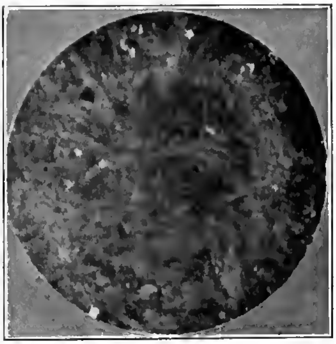

Fig. 19.
10% PbS + 90% Sb_2S_3

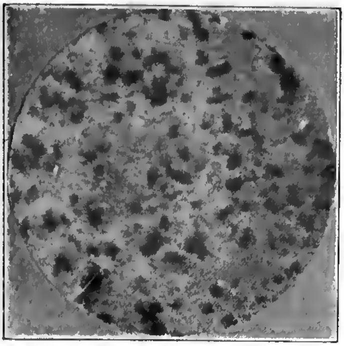

Fig. 21.
90% Ag_2S + 10% As_2S_3.

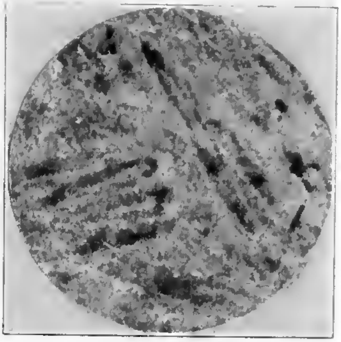

Fig. 22.
80% Ag_2S + 20% As_2S_3

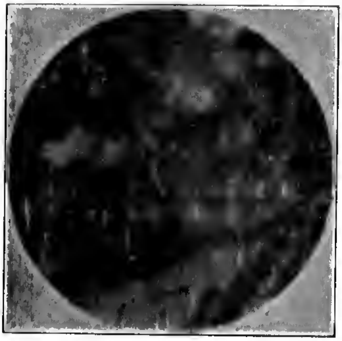

Fig. 23.
75% Ag_2S + 25% As_2S_3.
(Proustite.)

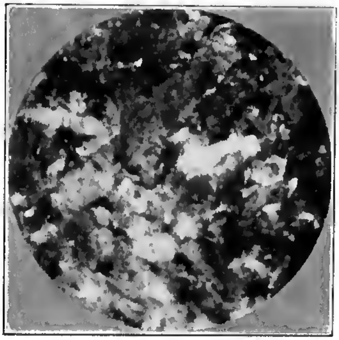

Fig. 24.
40% Ag_2S + 60% As_2S_3

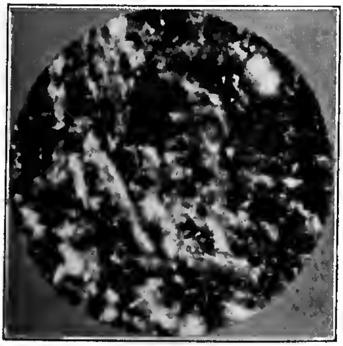

Fig. 25.
25% Ag_2S + 75% As_2S_3.
(with Na_2S.)

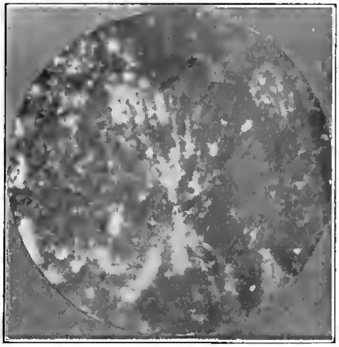

Fig. 26.
10% Ag_2S + 90% As_2S_3.

meta-acid, the jamesonite of the pyro-acid, while an ortho-sulphoantimonite is not known. There is a great variety of type, perhaps the formation of solid solutions, and one can expect, that the meltingpoint diagram will prove to be very complicated.

SECTION 12. Also here many investigators have tried to prepare these minerals artificially. *J. Fournet* [Journ. f. prakt. Chem. *2*. 129, 255,478, (1834); Ann. de Chim. et Phys. (1834). 412.] pretends to have obtained zinckenite by melting together $Pb\,S$ and $Sb_2\,S_3$, and sublimation of the superfluous $Pb\,S$. There is no evidence in his experiments, to suppose that he succeeded in this. In the same way *H. Sommerlad* (loco cit.) claims to have prepared (jamesonite, boulangerite, domingite and plagionite, by heating $Sb_2\,S_3$ with $Pb\,Cl_2$. That this is wrong is proved satisfactorily by *Ducatte* and *Rondet* (loco cit.).

SECTION 13. To get $Pb\,S$ in a pure state proved not to be a simple matter. First we tried to prepare it by precipitation of lead-acetate with $H^2\,S$; all $Pb\,S$ however, prepared in this way or from other solutions, contained too little Pb: we found commonly values below 80% Pb. Even after thoroughly drying, it always contains humidity, or it oxydises very rapidly at 100° and higher. The products of the trade are not better: a preparation of *De Haën* contained 78.25% Pb; if heated in a current of carbondioxyde, the substance lost 2.25% of weight.

This difficulty was already felt by *Friedrich* [Metallurgie, *2*. 536 (1905)], who investigated the binary system; $Pb\,S + Pb$, and who used finally the natural $Pb\,S$ as the best material. We have finally found a product of *De Haën*, molten and solidified to large, lustrous crystals; the analysis showed 86.3, resp. 86.4% Pb; only a few traces of iron were present as impurities.

The $Sb_2\,S_3$ used was obtained by solving the common red $Sb_2\,S_3$ in $Na^2\,S$, precipitation with hydrochloric acid and purification after *Henz* (See *Treadwell*, Quantit. Analysis). The analysis gave 71.03% Sb; the meltingpoint was 546° C. Finally we found an old preparation of *Kahlbaum* with about the same properties.

SECTION 14. For the determinations we used a small nickel-wire-resistance furnace; the protecting glass-tube of the thermoelement had at the lower part the form of a needle of constant length, to make sure that the contact place was always on the same height in the liquid. In spite of stirring, there always occur undercooling phenomena, which could not be fully avoided by inoculation of crystalgerms. All determinations were made in an atmosphere of carbondioxide; two curves of each mixture were studied, with total masses of 10 grammes.

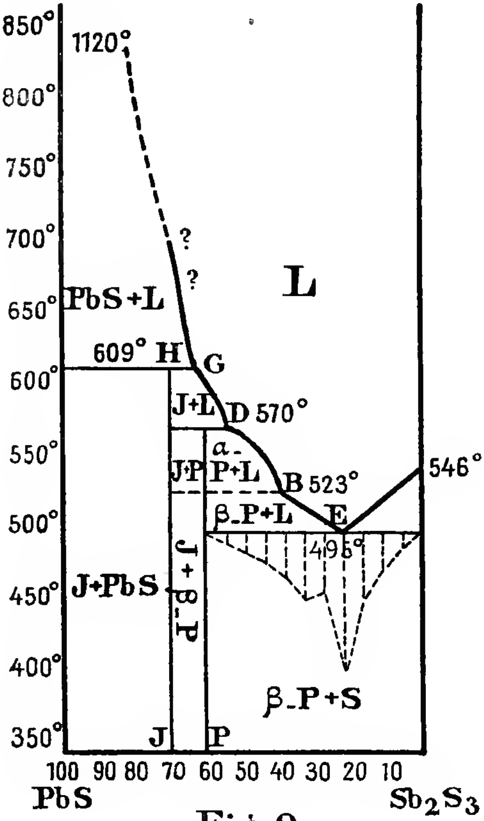

Fig. 9.

The obtained data are given below, and graphically represented in Fig. 9. It must be mentioned that the true explanation of these data was very much counteracted by the many retardation-phenomena.

BINARY MELTINGPOINTLINE OF LEADSULPHIDE AND ANTIMONYSULPHIDE

Composition of the mixtures		1st Heat Eff.		2nd Heat Eff.		3rd Heat Eff.		4th Heat Eff.	
Mol. Proc. Pb. S:	in Weight Proc. Pb. S		Time in sec.		Time in sec.		Time in sec.		Time in sec.
0	0	546°							
5	3.6	535°		454°	10°				
10	7.3	519°		464°	30°				
15	11.1	509°		481°	90°				
20	15.1	496°		496°	220°				
25	19.1	504°		480°	80°				
30	23.3	518°		480°	90°				
33.33	26.2	527°		470°	70°				
37	29.4	538°		464°	60°				
40	32.1	550°		467°	60°				
45	36.8	564°		450°	40°				
50	41.5	570°		490°		430°	30°		
52	43.5	574°		555°		519°		400°	20°
54	45.5	582°		560°		510°		391°	10°
55.55	47.0	590°		565°		522°		392°	
57.5	49.1	595°		564°		504°			
60	51.6	605°		573°		522°			
62	53.7	630°		610°		565°		470°	
63.63	55.4	655°(?)		606°		540°			
66.67	58.7	690°(?)		600°					
70	62.3	?		597°					
71.43	63.9								
75	68.1	?		586°					
80	74.0	?		582°					
83.3	78.0								
90	86.5			547°					
(100)	(100)	(1120°) (1)							

In every case we are sure now that there are two compounds, instable at their meltingpoints, which crystallize in a form closely analogous to that of the natural products. The transition-temperature (H) of *jamesonite* is situated at 609° C; that of *plagionite* (D) at 570° C. The last compound showed again a small heat-effect at about 523° C, which indicates a transformation in the solidified mass; we are not able to state this change by means of the microscope. The specific gravity of artificial jamesonite is determined pycnometrically at 5.62 (15° C.); that of the natural mineral is 5.68 - 5.70. For artificial plagionite we found 5.47; the natural product shows a density of 5.40.

However, we are of opinion that a compound, corresponding with zinckenite, is not formed: neither give the microscopical investigations any indication of this, but in the supposed case it would be expected that the inversion temperature of 523° C. should be observed in first instance in the mixture of 50%; however just there it was not to be found at all. The temperature of the fourth row cannot be explained in another way than of being those of the eutectic point *E*, but considerably lowered by increasing undercooling effects; these are connected with the very slight conductivity of heat in these liquids.

The normal situation of the eutectic point is at 495° C, and 80% antimonite.

Supposing that the cryscoptic constant of $Sb_2\ S_3$ is 791° C. it was calculated that the solved substance must be present in single molecules. The points of the branch at the *Pb S*-side could not be determined with high accuracy, because of the very small latent heat of fusion of the leadsulphide.

Section 15. A series of solidified masses was cut and polished, then etched with different liquids and microscopically investigated. The difficulty here is caused by the relatively feeble reflecting power of the surfaces, and by the impossibility, to get good polished surfaces at all. The enlargements are 25 times; the photographs were taken with the light of the electric arc.

Figures 10 - 15 represent masses, etched by hydrochloric acid. Figs. 10 and 11 show the *PbS* as primary crystallisation, Fig. 12 is almost that of an homogenous product, i. e. jamesonite; in Figs. 13 and 14 jamesonite is present with plagionite; in Fig. 15 almost all is plagionite. The surfaces of Figs. 16-19 were etched with sodium-sulphide-solution; in Fig. 16 is visible plagionite with a small amount of other structural element; in Fig. 17 plagionite is again the primary crystallisation; in Fig. 18 the apparently homogeneous eutectic mixture is represented, which at a stronger enlargement certainly shows to be heterogeneous; in Fig. 19 finally the characteristic form of the radial crystallising antimonite is visible. Principally those facts are in agreement with the interpretation of the melting point diagram, as given before the temperature of 523° C. must be an inversion temperature of an a-plagionite in a B-form, which cannot be discerned microscopically and no indication is present of the formation of another compound.

SECTION 16. As in the case of the silversulphoantimonites, we are here also forced to conclude that the corresponding natural minerals cannot be formed from binary molten magmas, but they have taken their origin by pneumatolytic and sedimentary processes, under the influence of volatile solvents.

SILVERSULPHIDE AND ARSENICSULPHIDE

SECTION 17. In connection with our determinations of the solid phases, which can be in equilibrium with binary liquids of silversulphide and antimony-sulphide, we have investigated in an analogous way the binary system of silversulphide and arsenicsulphide. We used silversulphide of *Kahlbaum*, dried in an atmosphere of carbondioxide at 300° C. The arsenic-sulphide was prepared from pure arsenic and the calculated quantity of sulphur; they were ground and mixed together, the mixture heated to 400° or 450° C. for several hours in a sealed glass tube, with a steady shaking of the mass. The homogeneous, but glassy product was powdered, analyzed and then used for the preparation duct was powdered, analyzed and then used for the preparations of the different mixtures. Precipitated arsenictrisulphide could not be used, because it always contains traces of acid, and other impurities which can be eliminated only at higher temperatures in open vessels where the danger of oxidation and vaporization of some sulphur was always present.

It may be mentioned here, that besides the experiments of *Sommerlad*, Z. f. anorg. Chem. *15*. 173. (1897); *18*. 420 (1898), also *Berzelius* says to have been able to prepare $Ag\ As\ S_2$ from solutions (Pogg. Ann. *7*. 150). One of *Sommerlad's* products seems to be identical with our *arsenomiargyrite*.

The binary mixtures were heated in small furnaces of nickelwire, and in an atmosphere of carbondioxide, to prevent oxidation as much as possible. These furnaces allow a cooling or heating of the mass in a very good way, much better than by means of the gas furnaces formerly used.

In the neighbourhood of pure $As_2 S_3$, no heat-effects could be observed, as the product always solidifies as a glass-substance. However, an amount of 10% $Ag_2 S$ is already sufficient to get a good crystalline product, and a very small heat-effect could be observed there at about 397° C. Generally, all liquids give good crystalline solid phases, with very coarse crystalline grains.

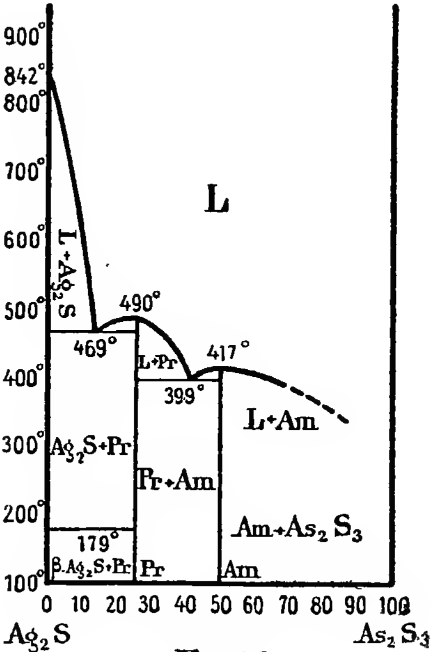

Fig.20.

The primary heat-effects of the crystallising $Ag_2 S$ are rather feeble in the cooling curves; in the heating curves they were hardly observable. The eutectic temperature was found constantly at 469° C. (+1°), but although it was very constant, this crystallisation effect was often noticed only after less or more retardation.

The inversion point of $Ag_2 S$ at 179° C. was not influenced in any considerable way by the presence of $As_2 S_3$; therefore, it seems that mixed crystals are not formed to any distinguishable concentration. The inversion point could be observed to an amount of $As_2 S_3$, of about 20%. The following data were found.

Binary Meltingpointcurve of Silversulphide and Arsenicsulphide

Composition in		Primary effect		Secondary effect		Transition temperature.
Mol. Proc. $As_2 S_3$	Weight Proc. $As_2 S_3$	on cooling	on heeting	on cooling	on heating	
0	0	842°	—	—	—	179°
5	5	715	—	454°	469°	179
10	9.9	610	—	463	469	179
15	14.9	502	—	469	469	179
17	16.9	469	469	—	—	179
20	19.9	481	—	467	469	179
25	24.9	490	—	—	—	
30	29.9	479	—	323	399	
35	34.8	445	—	399	399	—
40	39.8	398	399	—	—	—
45	44.8	414	—	394	399	—
50	49.8	417	417	—	—	—
60	59.8	413	413	—	—	—
66.67	66.5	410	410	—	—	—
75	74.9	407	408	—	—	—
80	79.9	404	407	—	—	—
90	89.9	351	397(?)	—	—	—
100	100	—	—	—	—	—

Section 18. As seen from the diagram Fig. 20 the behaviour of $As_2 S_3$ and $Ag_2 S$ to each other is wholly analogous to that of $Ag_2 S$ and $Sb_2 S_3$, formerly described. Here also there are two compounds: one, corresponding to pyrargyrite, and found in nature as *proustite* $Ag_3 As S_3$; the other one, corresponding to myargyrite, but not met with in nature, having the composition: $Ag As S_2$, which we will discern as *arsenomiargyrite*.

Proustite is homogeneously crystallised, solidifies without undercooling phenomena at 490° C., and possesses, if ground finely, a beautiful red colour, like sealing-wax, while the pyrargyrite under the same circumstances appears to be of a bright violet. The eutectic temperature between $Ag_3\,As\,S_3$ and $Ag\,As\,S_2$ lies at 399°; the eutectic mixture contains 40% $As_2\,S_3$. The compound $Ag\,As\,S_2$ melts homogeneously at 417° C., the maximum is very flat, and the substance seems to be dissociated in the liquid phase to a very high degree. The next mixtures become more and more viscous, and therefore also the undercooling phenomena get more and more noticeable, so that in the neighbourhood of the axis for $As_2\,S_3$, the observed effects are of considerably less value. Perhaps the melting point of $As_2\,S_3$ lies in the neighbourhood of 300° C.

On pure $As_2\,S_3$, in connection with the equilibria between As and S, (see the paper of *Jonker*, Zeits. f. anorg. Chem. *62*. 89. 1909.[1])

The microscopical investigation showed that *proustite* and *arsenomiargyrite* are both beautifully crystallized compounds. (Fig. 21 - 26). The proustite crystallizes in longshaped needles (Fig. 22 and 23); the arsenomiargyrite however in flat needles, or rather in plates (Fig. 25), which already microscopically present themselves as glittering spots much like mica, when the solidified mass is broken into pieces. The tendency to crystallize is a very great one, even in the cases where the amount of the $As_2\,S_3$ is very considerable. However in the Fig. 26 is shown the spherolithic structure of a mixture, rich in $As_2\,S_3$, as it is ordinarily found in cases of solidifying of undercooled magmas.

The *proustite* found in nature is wholly analogous to the artificial product. The specific gravity of the last was determined 5.51, while for the natural product values are given ranging from 5.5 till 5.6. The artificial proustite possesses the same colour and habitus as the mineral itself. For the arsenomiargyrite we found a specific gravity: 4.49 at 15° C.

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[1] The melting point of As_2S_2 was found to be 320°; that of As_2S_3 seems to be about 305° C.

PYRARGYRITE AND PROUSTITE

SECTION 19. Pyrargyrite and Proustite occur in nature as two minerals of very closely related forms, so that a direct isomorphy seems to be present. They are met with together, and occur commonly in juxtaposition; however, although pyrargyrite can possess two or three per cent. *As*,[1] and proustite as much Sb_2, true solid solutions of higher concentration of both minerals seems not to have been found till now, as chemical analysis shows. If crystals with greater concentration occur, there seem in most cases to be present mechanical conglomerations.

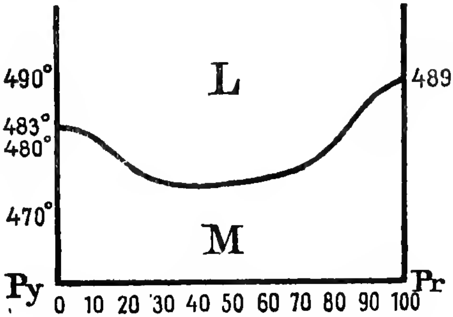

Fig. 27

These facts seem to be sufficiently important, to take up the problem, if real solid solutions in every proportion can be formed between the two minerals, or if only a partial miscibility in the solid state would be present.

SECTION 20. To investigate the mutual behaviour of both minerals to each other, we have determined the binary melting point line of very finely ground mixtures of both compounds. The pyrargyrite has a beautiful dark lilac colour, the proustite a bright red one, if they are present in the state of fine powders. Both substances have a very considerable velocity of crystallisation, as a result, also in binary mixtures they crystallise promptly, so that on stirring never any supersaturation phenomenon was observed; and even, if stirring was omitted, the undercooling never amounted to more than two or three degrees. The solidification points therefore could be used in this case with satisfactory exactness; we used a small nickelwound resistance-furnace, and all mixtures were melted in an atmosphere of carbon-dioxide. The temperature gradient of the furnace commonly did not exceed about two or three degrees in half a minute. The results are given below.

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[1] *Dana*, Mineralogy, 6th Ed., p. 133 (1909) gives for pyrargyrite: 0-3.8% *As*, and spec. w. varying from 5.90 till 5.68.

BINARY MELTINGPOINT OF PYRARGYRITE AND PROUSTITE

Composition in Mol. Proc.		Composition in Weight Proc.		Temp. of Solidification
Pyrargyrite	Proustite	Pyrargyrite	Proustite	
0	100	0	100	489.°5
5	95	5.4	94.6	487.°5
10	90	10.8	89.2	485°
15	85	16.0	84.0	483°
20	80	21.4	78.6	476°
30	70	31.9	68.1	476°
40	60	42.1	57.9	476°
50	50	52.2	47.8	475°
60	40	62.1	37.9	473.°5
70	30	71.8	28.2	475°
80	20	81.4	18.6	475.°5
90	10	90.8	9.2	481.°7
95	5	95.1	4.9	482.°2
100	0	100.	0	483°

SECTION 21. These data are graphically reproduced in the diagram Fig. 27 and show, as was further confirmed by the microscopical research etc. that the two minerals form a continuous series of solid solutions; the melting point line possesses a very flat minimum in the neighbourhood of 60 mol. proc. pyrargyrite, and shows a rather particular shape.

The temperatures differ only little from those of the pure components; the solidus line coincides practically with the liquidus curve, and is not well determinable: it seems however, that it nowhere deviates more than about 2° from the upper curve.

We have not been able to find other thermal effects at lower temperatures; so it seems that no hiatus in the mixing-series occurs on further cooling.

Of some preparations sections were made, so far as possible carefully polished, and studied by means of the microscope. It could be shown, that in every case only a single structure-element was present, which must be considered as being mixed crystals of both the components. They are relatively small, so that the preparation looks as if constituted by very fine grains. The above mentioned conclusion about the miscibility of both minerals, crystallizing from binary molten magmas, was thus really confirmed.

These facts prove once more that the circumstances, under which the simultaneous precipitation of proustite and pyrargyrite in nature have occurred, must have been quite different from the experimental ones. Evidently they cannot be formed in nature from binary magmas; so also here it seems certain, that only sedimentary and pneumatolytic processes can be the cause of the observed partial miscibility, met with in nature.

ETUDE DES PROPRIETES MAGNETIQUES DES ALLIAGES DU FER, DU COBALT, DU NICKEL ET DU MANGANÈSE AVEC LE BORE

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Les alliages étudiés, dont on trouvera la description dans les annales de chimie et de physique, série 8, t. 17, p. 145, 1909, fondent à des températures très élevées; lorsqu'on les chauffe dans l'air, ils s'oxydent très profondément et, même dans l'hydrogène, ils attaquent facilement la procelaine, la silice et jusqu'à la magnésie. Ils sont, de plus, très durs et très cassants et il est à peu près impossible d'en former des barreaux allongés. Comme ils sont, au contraire, très faciles à pulvériser, l'étude préliminaire de leurs propriétés magnétiques qui fait l'objet de ce mémoire, a été faite sur les alliages réduits en poudre, dans des conditions aussi uniformes que possible.

Variation de la perméabilité magnétique avec la composition. Des poids égaux des alliages étudiés, pulvérisés et tamisés avec soin d'une manière uniforme, ont été successivement introduits dans un même tube de verre et tassés sans compression, jusqu'à volume invariable pour chaque échantillon. Le tube de verre a été introduit dans une bobine magnétisante et l'on a mesuré par la méthode balistique les variations du flux d'induction qui se produisaient lorsqu'on interrompait le courant inducteur.

Les alliages de fer et de bore ont donné les résultats suivants, Δ désignant la déviation du galvanomètre:

	mm
Fer doux, limaille brillante	Δ = 142
Fer doux, limaille superficiellement oxydée	139
Alliage à 1,4% de Bore	145
Alliage à 3,2, eutectique	158
Alliage à 5	167
Alliage à 5,8	172

	mm
Alliage à 8,9, Fe_2B presque pur	180
Fe_2B pur, cristaux isolés par voie chimique superficiellement oxydés	178
Alliage à 9,4% de Bore	175
Alliage à 9,9	173
Alliage à 12,6	168
Alliage à 14,9	130
Alliage à 20,9	112
Déviation due à la bobine seule	110

Si l'on porte en abscisses la teneur des alliages en bore et en ordonnées les déviations du galvanomètre proportionnelles à la perméabilité magnétique, le magnétisme rémanent des alliages pulvérisés étant à peu près nul, on obtient une courbe qui présente un maximum pour la composition de l'alliage défini Fe_2B. Le traitement chimique qui a permis de séparer ce corps produisant une légère oxydation superficielle, il est naturel de trouver pour la perméabilité des cristaux isolés une valeur un peu plus faible que celle de l'alliage le plus perméable, dont la composition est sensiblement la même mais qui n'a subi aucun traitement chimique; on trouve d'ailleurs, une différence du même ordre entre la limaille de fer brillante et oxydée. Il est intéressant de constater que le borure Fe_2B possède une perméabilité un peu supérieure à celle du fer doux. On pourrait objecter que les grains d'alliage pulvérisé peuvent avoir, à grosseur égale, une forme différente des grains de limaille produits par arrachement et qu'on ne doit pas conclure des poudres ainsi obtenues aux métaux massifs: mais, comme, dans les alliages à teneur croissante en bore depuis 1,4 jusqu'à 8, 9 où la ferrite et le borure Fe_2B sont juxtaposés, et qui sont comparables entre eux, la perméabilité croit avec la teneur en Fe_2B, il est légitime de conclure que la perméabilité de ce composé est supérieure à celle de la ferrite. L'étude de ces alliages est reprise actuellement suivant les méthodes de M. P. Weiss.

Il n'a pas été fait de mesures semblables avec les alliages de cobalt et de nickel qui n'avaient pas été préparés en quantité suffisante. Alors que l'addition de Bore au fer augmente sa perméabilité, un examen sommaire montre que le contraire a lieu pour le nickel, du moins à la température ordinaire: le borure Ni_2B n'est pas attiré par un fort aimant.

Les propriétés magnétiques de quelques composés du manganèse ont été signalées par Heusler (Zeit. & angew. ch., t. *17*, p. 260, 1904); Wedekind en a fait d'abord une étude rapide (Zeit. Electroch., t. *11*; p. 850, 1905) complétée plus tard. (Zeit. f. physik. chem., t. 66, p. 614, 1909) par des mesures relatives à la perméabilité, à la saturation magnétique et à l'hystérésis des composés définis.

J'ai étudié la variation de la perméabilité avec la composition dans les alliages du manganèse avec le bore par la méthode employée pour les alliages de fer: les résultats obtenus ont été tes suivants, Δ désignant la déviation du galvanomètre balislique dans les mêmes conditions:

Alliage à 1,4%	$\Delta =$	0
Alliage à 4		0
		mm
Alliage à 7,7		118
Alliage à 10		125
Alliage à 12,9		132
Alliage à 15,5		128
Alliage à 16,1		126
Composé défini MnB (16,66%) isolé chimiquement et superficiellement oxydé		127
Alliage à 17,3%		117
Alliage à 17,8		116
Alliage à 19,4		111
Alliage à 21		110
Composé défini MnB_2 (28,6%)		110
Limaille de fer brillante		142
Limaille de fer oxydée		139
Déviation dûe à la bobine seule		110

L'examen des deux composés définis MnB et MnB_2 montre que, seul, le premier possède des propriétés magnétiques qui n'appartiennent pas, non plus, au manganèse pur. La courbe des perméabilités présente un maximum entre les teneurs de 13 et de 15%, alors que le composé défini magnétique MnB est à

16,66%; cela tient à la présence dans les alliages à plus de 15%, fortement trempés par suite de leur mode de préparation au four électrique à tube, d'une petite quantité de borure MnB_2 non magnétique: Enfin, le traitement qui permet d'isoler MnB, oxydant superficiellement les cristaux, on peut faire, à son sujet, la même remarque que sur le borure Fe_2B.

Variation de la perméabilité avec le champ. Pour les alliages du fer ou du manganèse qui ont été étudiés, l'induction a pris des valeurs très exactement proportionnelles au champ jusqu'à la limite des expériences (champ de 300 unités environ).

Magnétisme rémanent et hystérésis. Lorsque, après avoir coupé le courant magnétisant, on retire brusquement de la bobine le tube contenant l'alliage, on n'observe de déviation sensible (voisine de 1^{mm}) dans le galvanomètre balistique qu'avec les alliages de manganèse à grande perméabilité qui paraissent seul présenter un faible magnétisme rémanent. La limaille de fer doux donne, dans les mêmes conditions, une déviation de $2^{mm}5$.

Des expériences directes ont confirmé ce résultat: On fait passer, suivant la méthode de Braun, un pinceau délié de rayons cathodiques dans le champ résultant de deux paires de bobines, deux à deux identiques et placées sur le prolongement l'une de l'autre, dont les axes, faisant entre eux un angle droit, sont situés dans un plan perpendiculaire au faisceau cathodique. Deux de ces bobines, identiques et de même axe, sont enroulées dans le même sens et produisent sur le faisceau une déviation proportionnelle au champ inducteur; les deux autres, enroulées en sens inverse l'une de l'autre sont ajustées de façon que leur action se compense exactement. Si l'on place alors dans l'une de celles-ci l'un des alliages à étudier, la symétrie est détruite et le faisceau cathodique subit une déviation rectangulaire avec la première et proportionnelle à l'induction dans l'alliage. Lorsque les quatre bobines sont parcourues par un courant alternatif, on observe directement, sur un écran fluorescent placé sur le prolongement du faisceau cathodique, une courbe d'hystérésis de l'alliage.

Dans ces conditions, les alliages de fer et de bore, de manganèse et de bore, les borures Fe_2B, MnB, MnB_2 et CoB donnent des cycles plus aplatis que la limaille de fer doux.

Variation de la perméabilité avec la température. Points de transformation. Le perméabilité des alliages de fer, de cobalt et de manganèse diminue quand la température s'élève: on le constate en suspendant à un fléau de balance, à l'intérieur d'un tube de porcelaine vertical chauffé latéralement, un fragment d'alliage attiré par un aimant. Cette méthode ne donne que des indications sur les points de transformation, à cause des incertitudes sur la température. Ils ont pu être déterminés directement de la manière suivante: Une petite quantité de borure de fer pulvérisé est placée dans un tube de verre ou mieux de quartz de 5 m/m de diamètre parcouru par un courant d'hydrogène, entre les pièces polaires en cobalt d'un fort aimant qui peuvent être chauffées sans inconvénients jusqu'à 1000°: les grains d'alliage forment des chaînes très nettes suivant les lignes de force. Un couple thermo-électrique formé d'un fil de platine et d'un fil de platine rhodié traverse le tube d'un bout à l'autre suivant l'axe, la soudure se trouvant au milieu des grains d'alliage: on chauffe progressivement le tube et on note la température à laquelle se produit la désagrégation des chaînes: pendant le refroidissement, si l'on prend soin de frapper de légers coups sur le tube, on voit les chaînes se reformer à une température un peu inférieure à la précédente. On a trouvé ainsi les résultats suivants:

	Fe_2B	Fer doux
Disparition du magnétisme à température croissante	740°	800°
Réapparition du magnétisme à température décroissante	730°	760°

Pour les alliages de cobalt et de manganèse avec le bore, les températures de transformation, beaucoup plus basses, ont pu être déterminées plus simplement (voir Le Châtelier et Wologdine, comptes rendus, t. 148, p. 776, 1909). Les alliages ont été mis en suspension dans un tube à essais dans l'huile de vaseline: un thermomètre servait d'agitateur: on peut déterminer à 1° près la température à laquelle les grains d'alliage cessent de rester en suspension dans le champ magnétique. On a trouvé ainsi, pour le point de transformation du borure de manganèse MnB: 260° et pour celui du borure de cobalt Co_2B: 156°.

On voit que le borure de fer et le borure de cobalt ont des points de transformation respectivement plus bas que le fer et le cobalt: en particulier, pour le cobalt dont le point de transformation est voisin de 1100°, l'abaissement est considérable. On pouvait se demander si, la combinaison du nickel avec le bore ayant produit un abaissement semblable (point de transformation du nickel 340°), le borure de nickel Ni_2B, non magnétique, à la température ordinaire, ne se trouvait pas au dessus de son point de transformation; on pouvait espérer trouver celui-ci aux basses températures. Aucune attraction par un fort aimant n'a pu cependant être observée, jusqu'à la température de l'air liquide.

SUR LA RÉDUCTION DU PHOSPHATE TRICALCIQUE PAR L'HYDROGÈNE

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Les travaux relatifs à la réduction des phosphates par les réducteurs gazeux sont anciens et peu nombreux.

En 1860, Struve[1] réduisit par l'hydrogène les phosphates terreux avec formation des phosphures, et les phosphates alcalino-terreux, avec production des phosphates tribasiques. Il opérait à une température qu'il dit être celle du rouge blanc, et dans ces conditions les phosphates alcalino-terreux tribasiques ne subiraient aucune réduction. En 1864 Schloesing[2] reconnut que le phosphate de chaux et celui d'alumine mélangés de silice sont réduits par l'oxyde de carbone avec départ de la totalité de leur acide phosphorique, mais la silice est absolument indispensable à la réaction.

J'ai été amené incidemment, à étudier l'action de l'hydrogène sur le phosphate tricalcique, et j'ai reconnu que ce corps subit une réduction complète, assez facilement, avec production de phosphore et de chaux. J'ai opéré au four Heraüs, et les températures ont été relevées à la pince thermo-électrique.

Dans ces fours électriques, les températures sont très inégalement réparties, dans le four que j'ai employé, qui mesurait 34cm de longueur, il n'y avait au voisinage du centre qu'une région longue de 8cm dans laquelle la température ne variait pas de plus de 40°. C'est dans cette zone que j'ai placé la nacelle et la pince.

J'ai rencontré quelque difficulté dans le choix de la matière constituant la nacelle. La porcelaine subit à 1200° une altération profonde dans l'hydrogène, elle noirçit les silicates qui la constituent, perdant un atome d'oxygène pour chaque atome de métal qu'ils renferment; le charbon perd notablement de son poids en donnant du méthane; la silice ne varie pas de poids, mais subit une transformation qui lui ôte toute résistance. Il n'y a que la magnésie qui résiste convenablement.

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[1] Struve. Journal für Praktische Chemie 79-348-1860.

[2] Schloesing. C. R. 59-384-1864.

Le Phosphate que j'ai employé a été obtenu par saturation de l'acide orthophosphorique par un lait de chaux pure. Il titrait 42% de P_2O_5 au lieu de 45,8% pour P_2O_53CaO. Le phosphate ainsi préparé renferme toujours un excès de chaux. La réduction commence à être sensible entre 900 et 1000°, le phosphate chauffé 4 heures, à 1000° a subi une perte de poids de 2,6%.

La réaction ne devient un peu rapide, qu'aux environs de 1300°. C'est la température à laquelle je me suis tenu dans mes essais.

J'ai procédé par chauffes de 6 heures dont on trouvera le résultat dans le tableau ci-dessous:

Temps	Perte	Perte totale	Fraction de Po^{25} total %
6 heures	15,1	15,1	35,9
12 heures	11,5	26,6	63,3
18 heures	8,7	35,3	84,5
24 heures	3,6	38,9	92,6
30 heures	1,5	40,4	96,1

Comme on le voit, au bout de 18 heures, plus des $\frac{3}{4}$ de l'acide phosphorique ont été volatilisés. Le phosphore produit, mélange des variétés blanche et rouge se condense dans la partie froide du tube de porcelaine dans lequel on chauffe la nacelle. Ce phosphore dissous dans l'acide azolique et précipité à l'état de phosphate-ammoniaco magnésien, ne représente guère que les $\frac{2}{3}$ de celui correspondant à la perte de poids de la nacelle, le reste a réagi sur les parois du tube de porcelaine qui est attaqué de la manière la plus vive. Le produit réduit se présente sous la forme d'une poudre blanche, très alcaline au tournesol, sentant fortement l'hydrogène phosphoré, bien que je n'ai pu y déceler de quantité appréciable de phosphure de calcium qui ne doit pas prendre naissance en présence de vapeur d'eau. Ce produit n'a aucun pouvoir réducteur vis-à-vis du sulfate de cuivre et du nitrate d'argent, ce qui exclut la formation du sel de calcium d'un acide moins oxygéné que l'acide phosphorique. Les gaz sortant du four, pouvant renfermer de l'hydrogène phosphoré, en petites quantités, ont été dirigés dans des laveurs à nitrate d'argent. J'ai recueilli ainsi des quantités de phosphore extrêmement faibles, ce qui semble évident, l'hydrogène phosphoré ne devant se trouver, à cette température, qu'en très petites proportions dans le mélange gazeux.

Je me suis demandé, si la réduction du phosphate de chaux donnait du phosphore et de la chaux ou si l'on passait par une succession de phosphates basiques. Dans ce but j'ai analysé des phosphates partiellement réduits, en dosant la chaux libre, la chaux combinée et l'acide phosphorique. Le produit de la réduction est évaporé avec une solution de carbonate d'ammoniaque jusqu'à constance de poids, par calcination, on obtient une perte de poids correspondant à l'acide carbonique qui s'est combiné à la chaux libre, la chaux totale est ensuite dosée, ainsi que l'acide phosphorique.

J'ai opéré sur deux produits ayant subi, l'un une réduction d'une durée de 6 heures, l'autre de 18 heures.

Composition du produit réduit:

Durée de la réduction	Chaux libre	Chaux combinée	Anhydride phosphorique
6 heures	8,8%	53,1	38,0
18 heures	51,5	29,4	18,9

Le phosphate restant dans le produit réduit se trouve avoir la composition suivante:

	CaO	PO^{25}
après 6 heures	58,2%	41,7%
18 heures	60,8%	39,1%

Ces résultats ont été obtenus avec du phosphate précipité renfermant:

CaO	P^2O^5
54,3%	45,7%

On voit donc que le phosphate qui reste, à coté de la chaux libre, n'est pas du phosphate tricalcique pur, mais probablement un mélange de celui-ci avec un produit plus basique.

J'ai effectué dans les mêmes conditions la réduction de la cendre d'os, qui s'est comportée de la même manière que le phosphate précipité. Ayant obtenu ces résultats avec l'hydrogène, je pensais pouvoir employer avec le même succès l'oxyde de carbone, celui-ci ayant à peu prés le même pouvoir réducteur que l'hydrogène, en effet $H_2 + O$ dégage 58 calories et $CO + O$ en dégage 68. L'oxyde de carbone, à 1300°, ne m'a donné aucune réduction, il est probable qu'on se trouve à une température où le frottement est suffisamment fort pour empêcher la réaction, il faudrait avoir recours à un catalyseur, pour diminuer les résistances passives.

DISODIUM MONOHYDROGEN PHOSPHATE AND ITS HYDRATES. THEIR SOLUBILITIES AND TRANSITION TEMPERATURES

BY ALAN W. C. MENZIES AND EDMUND C. HUMPHERY
University of Chicago, Chicago, Ill.

This work was undertaken, in continuation of other similar work, as the existing data are old and surprisingly discordant. The results of Poggiale (1844) and of Mulder (1864) are to be found tabulated in the literature. Above 50°, Mulder's solubility curve is concave towards the temperature axis.

By the help of a worm stirrer, saturation was usually attained within one hour. The samples of solution were analysed in duplicate by weighing as anhydrous orthophosphate and subsequent conversion to pyrophosphate. Any divergences in composition of the solid phases from orthophosphate would thus make themselves evident by a discordance between the two analyses. Means were devised to isolate and dry for analysis the solid phase appropriate to each branch of the solubility curve at the temperature of its formation. To avoid the possible partial dehydration of the hydrates isolated that would result if ordinary air were employed for drying, the air current used was rendered suitably humid by bubbling through a saturated solution of the salt maintained at a temperature but a few degrees below that of the crystals to be dried. For maintaining the solubility vessel at elevated temperatures constant to hundredths of a degree, a very convenient vapor thermostat was afforded by the outer jacket of the molecular weight apparatus described by Menzies.[1] For lower temperatures a water tank thermostat was used, while, for the temperature 120°, an oil bath was maintained constant by hand. At this high temperature, also, saturated solutions were obtained by rocking solution and solid in a sealed glass tube furnished with a terminal bulblet whose neck was at right angles to the axis of the tube. A portion of the clear liquor, for analysis, could be decanted into the bulblet at the constant high temperature, and the contents subsequently weighed and analysed by severing the bulblet from the tube after cooling.

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[1] J. Am. Ch. Soc., **32**, 1615, (1910).

It was found that disodium monohydrogen phosphate cannot safely be dried at 180° as stated in the literature,[1] because water of constitution of slowly lost at this temperature. Drying at about 95° is entirely satisfactory and is not tedious if the proper procedure is observed. In order to dry the powdered dodecahydrate, for example, this salt must be heated first at a temperature short of its melting point (35°), so as to take advantage of the rapid loss of water from the vast surface of the solid which would be enormously reduced if melting occurred. After half an hour in a well-ventilated crucible at this temperature, the drying of a one gram sample may be completed, by raising the temperature to about 95°, in less than two hours. To obtain most quickly anhydrous orthophosphate from a weighed quantity of its solution, this must not be evaporated continuously at 95°. The substance must first be converted, by evaporation finally below 35°, to dodecahydrate, which is then dried, after pulverisation, as above described.

The solubility data tabulated below are in terms of parts of anhydrous Na_2HPO_4 per 100 parts of water. The figure represents these results graphically. The temperature scale was defined by a platinum resistance thermometer, and the temperature measurements are believed to be accurate to tenths of a degree, except at 120°, where the error may be half a degree.

The transition temperatures dodecahydrate—heptahydrate and heptahydrate—dihydrate were determined directly by the dilametric method.

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[1] Cf. Whitlock and Barfield, *Am. Chem. J.*, **22**, 214, (1899).

Solid Phases	Temperature	Parts Na_2HPO_4 in 100 parts water
Ice[1]	— 0.43	1.42
	— 0.24	0.70
Cryohydric point	— 0.5	
Dodecahydrate	+ 0.05	1.67
	20.0	7.66
	25.0	12.0
	32.0	25.7
	34.0	33.8
Transition temperature	35.2	
Heptahydrate	39.2	51.8
	45.0	67.3
Transition temperature	48.3	
Dihydrate	50.0	80.2
	60.0	82.9
	80.0	92.4
	90.2	101.0
Transition temperature	95	
Anhydrous Na_2HPO_4	96.2	104.6
	105.0	103.3
	120	99.2

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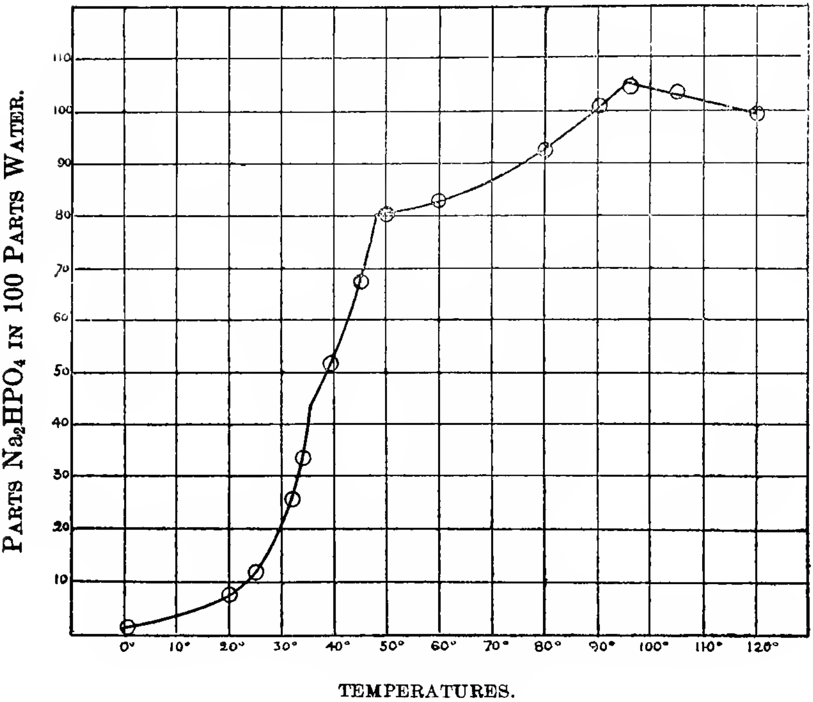
[1] Values recalculated from the work of Jones, *Hydrates in Aqueous Solution*, p. 39, table 14.


PARTS Na_2HPO_4 IN 100 PARTS WATER.
110
100
90
80
70
60
50
40
30
20
10
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
100°
110°
120°
TEMPERATURES.

THE RETENTION OF SMALL QUANTITIES OF WATER BY ARSENIC PENTOXIDE AT ELEVATED TEMPERATURES

By Alan W. C. Menzies and Paul D. Potter

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It is well known that the last traces of water are removed from certain substances with great difficulty even at elevated temperatures. In converting the hydrate $3As_2O_5, 5H_2O$ to arsenic pentoxide it was found that the greater part of the water is quickly removed; the last portions of water, however, were apparently retained more strongly, although by no means so insignificant in amount as to be difficult to determine satisfactorily. Further study was therefore made of this favorable case in the hope of throwing light on the way in which such small quantities of water are attached to the anhydrous material.

It should be mentioned that the statement of Auger,[1] that the dehydration of the hydrate $3As_2O_5, 5H_2O$ is complete at temperatures so low as 180°, and the method of Balareff[2] of analysing the same hydrate by ignition for three hours at 200°, are both out of harmony with the results described below.

A quantity of 2.4723 grams of the above-mentioned hydrate, when heated in a glass tube for 293 hours at 155° in a current of dry air reached "constant" weight while still containing 1.05% of water. By " constant " weight is here meant that the rate of loss of weight for the last 100 hours of heating was 0.00005 g. per hour. The temperature was then raised successively to 170°, 187°, 208° and 238°, when the water remaining at " constancy " was 0.85%, 0.77%, 0.54% and 0.42%. The table below indicates (2) the total number of hours of heating at each temperature, (3) the actual weight of material remaining, (4) the percentage of water remaining in the material, (5) the final rate of loss per hour, (6) the number of hours of final heating used in estimating (5).

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[1] Compt. rend., **146**, 585 (1908).

[2] Z. anorg. chem., **71**, 73 (**1911**).

1	2	3	4	5	6
25°	0 hrs.	2.4723 g.	11.55%		
155°	293	2.2101	1.05	0.00005 g.	100 hrs.
170°	99.3	2.2056	0.85	0.00001	26
187°	138.8	2.2037	0.77	0.00001	72
208°	219.5	2.1987	0.54	0.0000	96
238°	235.0	2.1961	0.42	0.000004	119

It was shown that the losses of weight occurring corresponded exactly with the gains of weight of a water absorption tube.

The experiment at 170° was confirmed by repeating with three portions of the starting material in as many crucibles in ordinary winter air. Air containing 8 mm. aqueous tension, when passed for 48 hours over the residues maintained at 170°, caused no gain in weight. Air containing 20mm. aqueous tension likewise failed to cause change in weight in 20 hours at this temperature. Twenty-five milligrams of the starting material were then added to the residue in one crucible, in order to induce, by inoculation, the initiation of rehydration at 20mm. humidity. After 45 hours at 170°, however, in a current of air of this humidity, the added material had arrived at the same degree of dehydration as the rest of the contents of the crucible.

A sample of the starting material ($3As_2O_5$, $5H_2O$) was then heated at 170° in a current of air containing 20 mm. of aqueous tension. In 133.3 hours it had become further dehydrated than the samples dehydrated for longer periods in drier air in the previous experiment.

After a number of confirmatory experiments had been made at the temperature 210°, the effect at 170°, of air of 300 mm. aqueous tension was now tried upon the final residues left on drying to " constant " weight in ordinary air at 170°. This was found to produce a very marked further dehydration. It was, of course, shown that empty crucibles similarly treated did not lose weight. Final conversion to arsenic pentoxide at 250° gave values varying from those calculated from analysis of the starting material by the pentasulphide method by only 0.05%, 0.02%, 0.01% and

0.01% respectively of the quantities weighed for the four experiments made. This is evidence that no compound of arsenic had been volatilized by the steam.

Four samples of the starting material, when dehydrated at 170° in a current of air containing 300mm. pressure of water vapor gave, after only 61 hours, residues, not anhydrous but containing markedly less water than when drier air was used for 547 hours at the same temperature. Here, again, ultimate conversion at 250° to arsenic pentoxide showed that nothing but water had been lost.

It seems not unlikely that humid air could be profitably tried as a drying agent for obtaining substances anhydrous for atomic weight determination.

A number of further experiments readily suggest themselves, and some of these have been already made. In regard to the manner in which the small quantities of water are retained, however, the experiments quoted seem sufficient to show:

(1) The water is not superficial adsorbed water, for this would be increased and not decreased in quantity by using a high aqueous tension in the drying air.

(2) The water is not contained in cavities. Analysis of the starting material, $3As_2O_5$, $5H_2O$, showed that even this contains only negligible quantities of water beyond that demanded by the formula. In order that the anhydrous pentoxide should retain 0.72% of included water, about 2 per cent. of its weight would require to be made up of saturated solution of arsenic acid. For the purpose of obtaining an *anhydrous* residue free from cavity water, Richards[1] has recommended this very process of expelling water of hydration from a hydrated compound.

(3) It seems unlikely that the water could be present as water of hydration or constitution, for this would demand the existence of a large number of hydrates of compositions such as $12As_2O_5$, H_2O.

(4) The water may be present in solid solution or otherwise in the interior or granules from which its escape is prevented more or less effectively by the presence of an anhydrous or little

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[1] Proc. Am. Phil. *Soc.*, **42**, 28 (1903).

hydrous shell or rind. It will be recalled that Baker and Adlam[1] have shown that hydrated substances such as barium chloride dihydrate are pervious to water vapor, while anhydrous substances such as potassium dichromate are not. If the—at best very low—degree of hydration of the impervious shell is controlled jointly by the water concentrations within and without, it is evident that humid air may desiccate the entire material further and more quickly than dry air.

This investigation was carried out in the Kent Chemical Laboratory of the University of Chicago.

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[1] J. Chem. Soc. **99**, 507 (1911.)

SUR L'OXYDATION DE QUELQUES SUBSTANCES INORGANIQUES A HAUTES PRESSIONS ET TEMPÉRATURES

PAR JAROSLAV MILBAUER

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L'objet de mes recherches a été d'étudier l'action de l'oxygène à haute pression (12 atm.) et température (480° C.) sur différents oxydes de métaux ainsi que sur des mélanges intimes de ces oxydes. Les corps en question ont été traités par l'oxygène dans une bombe en fer pendant une heure dans les conditions déjà indiquées.

Voici ce que j'ai remarqué:

1. Les oxydes de lithium, de sodium et de potassium contenaient des peroxydes.
2. Les oxydes de glucinium, calcium, zinc, strontium et de cadmium n'ont pas subi d'altération.
3. L'oxyde de baryum s'est tranformé en peroxyde de baryum.
4. Les oxydes d'aluminium, bore, thallium, silicium, zirconium et d'étain n'ont pas reagi.
5. L'oxyde de plomb a donné du minium.
6. L'oxyde d'antimoine a été oxydé en tétroxyde.
7. L'oxyde de bismuth n'a subi aucun changement.
8. Le sesquioxyde de chrome contenait du chromate de chrome.
9. L'oxygène néxerce aucune action sur les oxydes normaux de Mo, Wo, Ur et Fe.
10. Les oxydes de cobalt et de nickel fournissaient des produits contenant une certaine quantité d'oxydes supérieurs.

Comme on voit il n'y a dans cette ction aucune anomalie, si l'on fait abstraction de l'oxyde d'argent. Je crois, qu'il se forme ici un oxyde supérieure, mais je ne l'ai pu isoler en quantité suffisante. L'oxyde d'argent traité par l'oxygène dans mon appareil fournit un produit qui se trouve apres l'ouverture du tube sur ses parois. C'est un mélange. C'est pourquoi j'ai renoncé à l'analyser. En soumettant une feuille d'argent à une action bien plus prolongée j'ai observé une couche noire qui degageait du chlore avec de l'acide chlorhydrique. Je me propose d'étudier cette réaction d'une manière plus détaillée.

Mon intention était aussi d'opérer avec d'autres mélanges intimes d'oxydes, mais je me suis borné pour le moment a ceux du sesquioxyde de chrome dans les conditions suivantes: La pression était de 12 atmosphères et la température de 460° C. pendant 60 minutes.

Je résume les résultats de mes recherches en ce tableau:

Mélange	Couleur avant le traitement	Couleur aprés le traitement	Analyse
$Ag_2O : Cr(OH)_3$	Brun-verdâtre	Brun-rougeâtre	100.0% Ag_2CrO_4
$BeCO_3 : Cr(OH)_3$	Vert pale	Jaune-verdâtre	8.5% Be_2CrO_4
$Mg(OH)_2 : Cr(OH)_3$	Gris-verdâtre	Jaune	82.7% $MgCrO_4$
$CaCO_3 : Cr(OH)_3$	Gris-verdâtre	Jaune-verdâtre	56.9% $CaCRO_4$
$Zn(OH)_2 : Cr(OH)_3$	Gris-verdâtre	Jaune-brunâtre	72.0% $ZnCrO_4$
$SrCO_3 : Cr(OH)_3$	Gris-verdâtre	Jaune-brunâtre	63.0% $SrCrO_4$
$Cd(OH)_2 : CR(OH)_3$	Vert pâle	Jaune	66.9% $CdCrO_4$
$BaCO_3 : Cr(OH)_3$	Vert pâle	Jaune-brunâtre	52.8% $BaCrO_4$
$Zr(OH)_4Cr(OH)_3$	Vert Pâle	Jaune-brunâtre	La substance contenait 1.9% d'oxygène actif.
$Ce(OH)x : Cr(OH)_3$	Jaune brunâtre	Brun violet	La substance ne subit aucun changement.
$PbCO_3 : Cr(OH)_3$	Vert	Jaune	100.0% $PbCrO^4$
$Sb_2O_3 : Cr(OH)_3$	Vert	Brun vert	La substance contenait 0.8% d'oxygène actif.
$Bi_2O_3 : Cr(OH)_3$	Vert	Brun vert	6.3% $(BiO)_2\ CrO_4$
$Cr(OH)_3$	Vert	Noir	La substance contenait 1.4% d'oxygène actif.
$Mn(OH)x : Cr(OH)_3$	Brun. La substance contenait 6.5% d'oxygène actif.	Noir	La substance contenait 9.6% d'oxygène actif.
$2Fe(OH)_3 : Cr(OH)_3$	Jaune brunâtre	Rouge brun	La substance contenait 1.2% d'oxygène actif.

$Ni(OH)_2 : Cr(OH)_3$	Vert	Brun	La substance contenait 4.8% d'oxygène actif.
$Cu(OH)_2 : Cr(OH)_2$	Vert	Rouge brun	5.3% $Cu\text{-}CrO^4$

Tous ces mélanges, exepté celui de $Ce(OH)_x$: $Cr(OH)_3$ absorbaient de l'oxygene et fournissaient des chromates. Dans le deuxième groupe du système périodique des éléments, la quantité d'oxygène absorbée diminue en raison inverse du pois atomique, à partir du magnésium jusqu'au baryum. Les chromates d'argent et de plomb se forme très facilement. On peut utiliser cette réaction pour la fabrication de couleurs minérales de chrome et de dels de l'acide chromique, comme par exemple du chromate de magnésium, qui peut remplacer dans bien de cas les chromates alcalins. Avant de finir je fais encore remarquer que j'ai demandé des brevets pour cette méthode.

Le présent travail a été éxécuté dans le laboratoire de l'Ecole polytechnique tchèque de Prague.

L'INDUSTRIE DU NITRATE DE SOUDE AU CHILI

PAR PROF. BELISARIO DIAZ OSSA

Santiago, Chile

Pendant de longues années, l'industrie salpêtrière chilienne est restée stationnaire dans son développement technique, seulement ces derniers temps ont apparu des signes certains d'une évolution, qui marquera une étape notable dans la transformation des procédés employés.

L'union des industriels nitratiers, ayant pour seul but de maintenir l'azote du nitrate de soude, à un prix de vente très élevé, a empêché l'étude et la transformation de la technique, car les méthodes d'élaboration du nitrate n'étaient que d'une importance secondaire; le prix étant très rénumérateur, les industriels n'avaient aucun intérêt à changer les procédés connus.

Ayant pris fin, le pacte qui liait entre eux les industriels nitratiers, le prix de vente du nitrate tomba, et alors, la lutte éclata pour produire au prix le plus bas. Les facteurs, plus importants, de cette évolution, ont été: le prix de vente décroissant de l'azote, et les exigences toujours plus grandes de la main d'oeuvre.

La première partie de l'évolution, fut la mécanisation de la plupart des opérations; toutes les usines " *oficinas* " ont perfectionné: leurs moyens de manutention mécanique, la production de l'énergie dont elles ont besoin, ont amélioré le rendement des générateurs de vapeur, introduit le pétrole comme combustible et électrifié tous leurs services.

La dernière partie de cette évolution, touche directement aux méthodes employés pour élaborer le nitrate, elles se trouvent actuellement en plein développement. Il faut citer surtout les résultats obtenus de l'évaporation des dissolutions du nitrate en appareils spéciaux.

La présente étude a pour objet de donner une idée de l'état actuel de l'industriel chilienne de l'azote et de faire connaître les nouvelles voies ouvertes à sa technique.

Le développement de l'industrie du nitrate de soude a commencé en 1830, époque à laquelle les premiers chargements de nitrate ont été exportés en Europe. Ce développement a été progressif et relativement lent; pourtant ces dernières années, l'exportation a atteint un chiffre élevé; il a été, en 1911 de 2,487,000 Tonnes, correspondant environ à 350,000 Tonnes d'azote, alors que le même année la production de sulfate d'ammoniaque, l'engrais azote artificiel plus répandu correspond seulement à 250,000 Tonnes d'azote.

La valeur commerciale du produit exporté en 1911 atteint 600,000,000 de francs, sur lesquels mon pays a prélevé comme droit d'exportation, la somme de 160,000,000 de francs.

L'industrie du salpêtre donne, en outre, comme sous produits, l'iode dont on exporte 500,000 Kgs, d'une valeur commerciale de 10,000,000 de franc, le perchlorate de potasse, le chlorure de sodium, etc.

Cette industrie a une importance particulière, à cause de la région du monde où elle se trouve située: en plein désert, sans aucune végétation, presque sans eau, loin des ressources nécessaires à la vie. Il a fallu tout créer, et porter à de longues distances tous les objets de consommation: le charbon, l'eau, les aliments pour les hommes, le fourrage pour les animaux, etc.

Le développement progressif de l'industrie a fait s'élever autour d'elle des villes importantes et nombreuses: Iquique, Antofagasta, Taltal, Tocopilla, pour ne citer que les principales; on a construit et on construit encore des chemins de fer et des moyens d'embarquement, le tout à grands frais pour assurer un facile transport aux produits de la région, ainsi qu'aux articles de consommation dont elle a besoin. On a ainsi créé de toutes pièces, une zône qui vit exclusivement de l'industrie du nitrate.

Il existe aujourd'hui 160 usines, en travail, qui occupent plus de 43,000 ouvriers et consomment annuellement environ 600,000 tonnes de charbon; la région du nitrate consomme d'énormes quantités de produits alimentaires, conserves et autres, puisqu'elle comprend, en tout, plus de 170,000 habitants.

La région salpêtrière s'étend depuis le parallèle 19° 30′. Sud jusqu'au parallèle 26°, formant une bande étroite à environ 70 Kilom. de la côte de l'Océan Pacifique et à une altitude moyenne de 900 mètres au dessus du niveau de la mer (fig. 1).

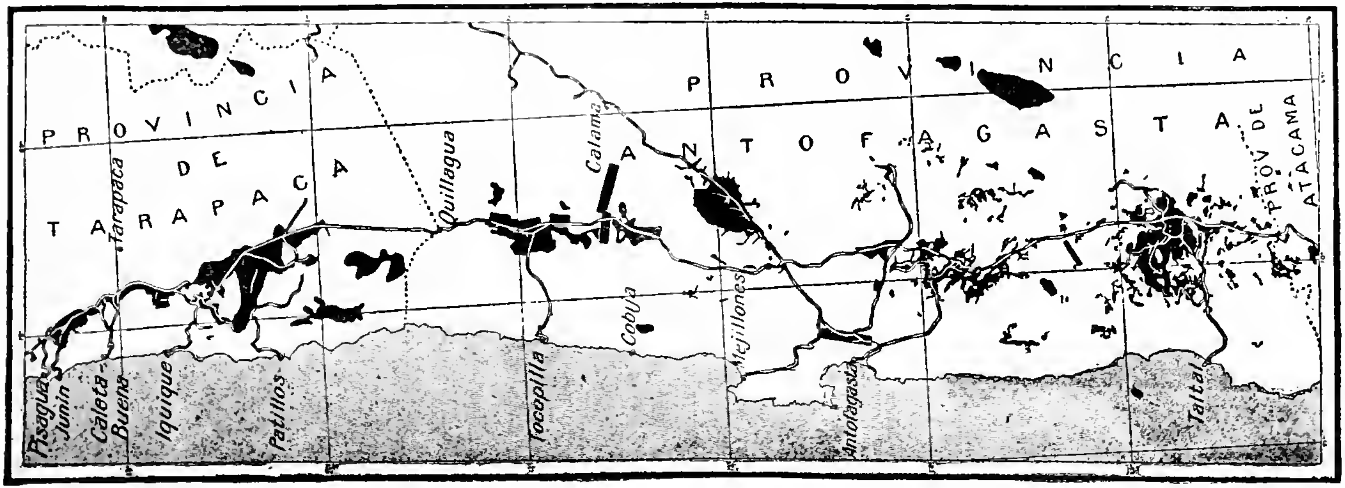
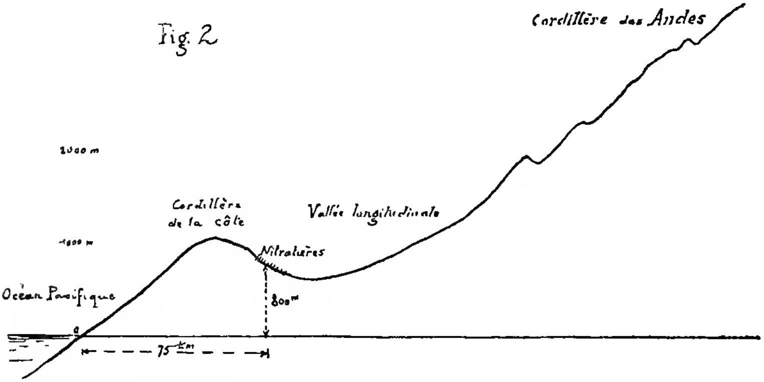

PROVINCIA DE TARAPACA
Tarapaca
Pisagua
Junin
Caleta-Buena
Iquique
Patillos
Quillagua
Tocopilla
Cobija
Calama
Mejillones
Antofagasta
PROVINCIA ANTOFAGASTA
Taltal
PROV DE ATACAMA

Figure 1

La formation la plus caractéristique se trouve dans la section TARAPACA; on peut se donner une idée de cette région par la coupe représentée (figure 2).

Fig. 2



La région salpêtrière est formée là de diverses parties bien distinctes: la Cordillère de la Côte, qui borde l'Océan Pacifique et se présente en certains points comme une muraille à pic comme à Caleta Buena et Junin, où l'on a du établir des plans inclinés rachetant des différences de niveau de 700 mètres; vient ensuite la vallée longitudinale, appelée Pampa du Tamarugal, puis les contreforts de la Cordillère des Andes, et enfin, cette même Cordillère et les Hauts Plateaux.

La région salpêtrière se trouve sur le versant intérieur, versant oriental, de la Cordillère de la Côte.

Plus au Sud, la vallée longitudinale disparait et est remplacée par des vallées transversales qui vont de la Cordillère à l'Océan et dans lesquelles se présente aussi la formation salpêtrière.

La région du nitrate, où il ne pleut jamais, est soumise à des vents constants pendant certaines saisons et à certaines heures du jour; à la tombée de la nuit, il se forme des brouillards épais, accompagnés de phénomènes électriques parfaitement sensibles; le terrain est radioactif à un très haut degré.

Le manque de toutes ressources et surtout d'eau, ainsi que la difficulté des communications n'ont pas permis, jusqu'à présent, une exploration systématique au point de vue géologique et géographique; on ne connaît que les points les plus accessibles. C'est pour cela qu'on ne peut décrire les gisements dans leur ensemble, ni déduire les lois générales de leur formation.

Lorsqu'on aura terminé le chemin de fer longitudinal Nord actuellement en construction, il sera plus facile de faire ces études et notre Gouvernement, qui ne néglige rien à ce point de vue, pourra les faire effectuer dans de meilleurs conditions qu'aujourd'hui.

De toute façon, il a été démontré que, rien que dans la partie déjà connue, il existe une quantité de nitrate suffisante à la consommation actuelle pendant un siècle.

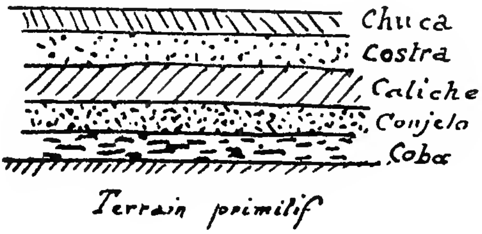
Le nitrate se présente sous les formes suivantes:

Couches, imprégnations et efflorescences, et remplissage de cavités dans le calcaire.

On exploite actuellement les couches, à l'exclusion des autres modes de gisement.

Une couche contenant du nitrate est formée par les assises indiquées dans la figure 3.

Fig. 3.



La *chuca* se compose de morceaux de quartz avec des sulfates anhydres de soude et de chaux; la *costra* contient déjà du nitrate, mais en moindre proportion que l'assise appelée " caliche; " elle atteint quelquefois 18% et sa composition est analogue à celle de la troisième couche.

Sous le nom de *caliche* on désigne aussi bien le minerai que l'assise qui le contient; celle-ci est formée de matières insolubles, sable, pierres, argile, agglomérées par un ciment de sels, formant ainsi un ensemble très dur.

Le *caliche* se présente sous diverses couleurs, blanc, jaune, gris foncé, bleu, violet; sa cassure est saccharoïde sa densité voisine de deux; la saveur est fraiche.

Sa composition en est très variable, ainsi que son épaisseur.

Le caliche contient: nitrate, chlorure et sulfate de sodium comme éléments principaux, et comme éléments secondaires; chlorure de potassium, sulfate et nitrate de calcium, chlorure, sulfate et nitrate de magnésium. On y rencontre aussi de l'iodate de sodium, le nitro-sulfate de sodium ou *darapskite,* l'iodate de calcium ou *lautarite,* l'iodo-chromate de calcium ou *dietzeite.*

L'analyse de deux échantillons de caliche et d'un autre de costra a donné:

	Caliche		Costra
Nitrate de soude	36	35	17
Chlorure de sodium	32	6	2
Sulfate de sodium	8	2	72
Insolubles	14	50	1
Sulfate de chaux	8	2	2
Autres sels	2	5	6

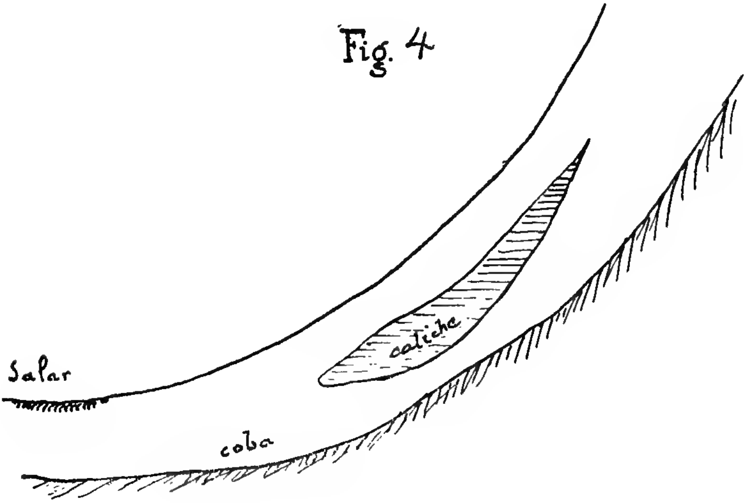
Comme règle générale, on peut dire que les caliches de la région du Nord, ou de Tarapaca, contiennent plus de chlorure de sodium que de sulfate, à mesure que l'on s'avance vers le Sud, le chlorure est remplacé par du sulfate, au point que les caliches de Taltal, le district le plus au Sud, contiennent plus de sulfate que le chlorure.

Les autres couches qui se trouvent sous le caliche ont peu d'importance; c'est le *congelo,* où dominent les chlorures et les sulfates, et la *coba,* formée de terre, de pierres et de très peu de sels.

Les diverses assises reposent sur le terrain primitif, c'est à dire sur les roches de la Cordillère, dont la nature ne paraît avoir aucune importance quant à la formation des dépôts de nitrate.

Dans le nord (Tarapaca), les couches de caliche se présentent sur le versant oriental ou intérieur de la Cordillère de la Côte, sur les petites élévations, à pente douce, qui bordent la vallée longitudinale. On trouve dans les parties les plus basses de cette vallée d'autres dépôts appelés *salares* (figure 4), qui se composent presque exclusivement de sel commun avec efflorescences de nitrate.

Fig. 4



Dans d'autres régions, plus au Sud (Antofagasta) les couches se présentent dans la partie la plus basse de la vallée transversale, et encore plus au Sud, à Taltal, on a trouvé des dépôts de nitrate jusque dans la partie la plus haute des montagnes, à 3000 mètres d'altitude.

On a formulé plusieurs théories pour expliquer la formation des dépôts chiliens; toutes ont le défaut de ne pas être générales, car elles ont été présentées au fur et à mesure que l'on connaissait des régions nouvelles. Aucune d'elles n'est aujourd'hui satisfaisante; ce n'est que lorsqu'on aura fait une étude complète, géographique et géologique, de toutes les zônes du nitrate que l'on pourra chercher une théorie qui explique sa formation.

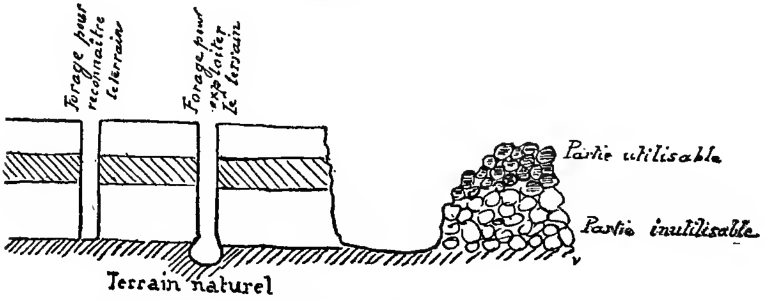
Noellner et Darwin admettent que l'azote du caliche provient des algues marines; Müntz et Plagemann croient à la nitrification microbienne; Ochsenius attribue la présence de l'azote au guano, dont il existe de grands dépôts le long de la côte de l'Océan Pacifique; Williams, Pissis et Sundt soutiennent l'origine atmosphérique, soit l'union de l'azote et de l'oxygène de l'air sous l'influence des décharges électriques.

La formation actuelle de nitrate, que l'on constate au fond des *salares* s'explique facilement par l'entraînement du nitrate des couches situées à flanc de coteau par l'eau condensée des brouillards; la dissolution se serait évaporée et, par capillarité, le nitrate serait monté à la surface du *salare* pour former des efflorescences; voir la figure 4.

Pour reconnaître, en vue de son exploitation future, un terrain à nitrate, on fait des trous, de distance en distance, à 50 ou 100 mètres les uns des autres, et on détermine ainsi l'épaisseur et la qualité de la couche de caliche.

Pour préparer l'exploitation, on élargit le fond du trou, on y verse une quantité suffisante de poudre au nitrate de soude et on fait détoner (figure 5). Les ouvriers, au moyen de marteaux et d'outils en acier, brisent les morceaux de roche; ils forment ainsi une tranchée qui leur permet ensuite d'extraire le minerai, en ayant soin de laisser le stérile en bas et de réunir dans la partie supérieure le caliche à traiter.

Fig. 5


Forage pour reconnaître le terrain
Forage pour exploiter le terrain
Partie utilisable
Partie inutilisable
Terrain naturel

L'ouvrier chilien reconnaît à simple vue le terrain salpêtrier de bonne ou mauvaise qualité et il se rend un compte exact de la teneur du caliche; s'il a un doute, il jette quelques morceaux de caliche moulu sur une mêche allumée et il juge de la teneur à la rapidité et a l'intensité de la déflagration.

Le caliche est transporté à l'usine soit dans des charrettes, soit au moyen d'une petite voie ferrée.

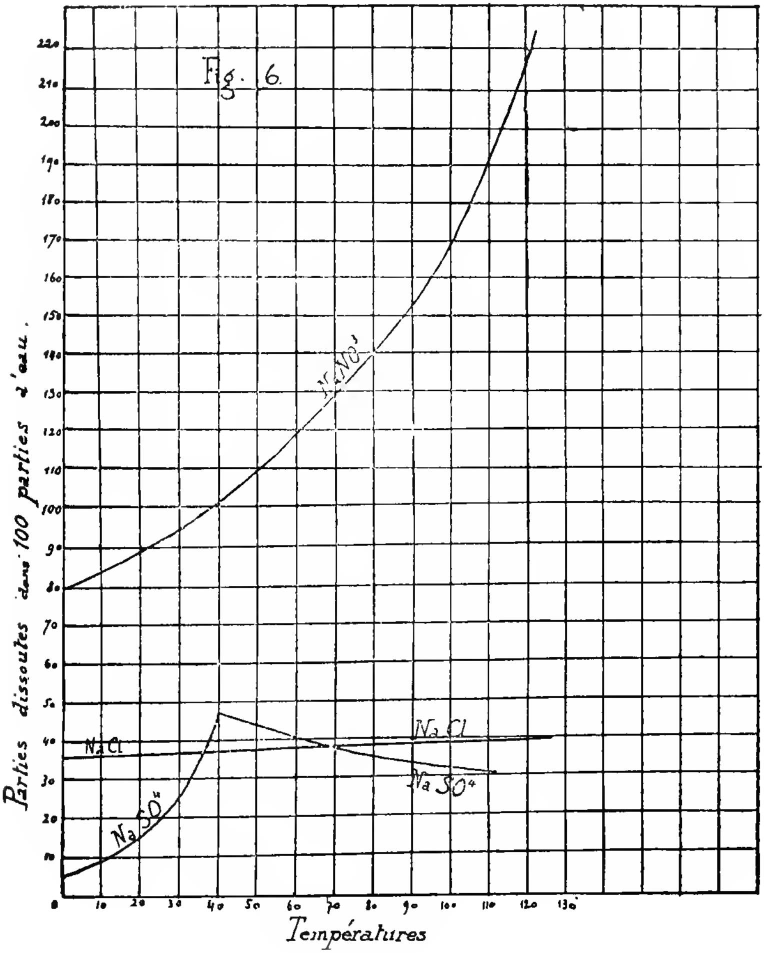


Fig. 6.

Le travail est fait à la tâche, et les ouvriers sont payés suivant le nombre de charrettes ou de wagonnets; on tient compte également de la teneur du caliche, de l'épaisseur de la couche utile, de la profondeur à laquelle elle se trouve et de la facilité plus ou moins grande à reconnaître le caliche des autres éléments.

Rarement, il est possible de faire avancer la tranchée parallèlement à elle-même; elle suit toujours la forme des couches. Les tranchées s'ouvrent d'habitude dans la partie la plus haute du terrain, en vue de faciliter le transport des matières extraites; elles progressent jusqu'à atteindre la partie la plus basse.

L'organisation du travail et l'établissement d'un plan d'exploitation sont d'une très grande importance pour l'obtention d'un bon résultat économique. Il faut tenir compte de trois facteurs principaux pour obtenir un bon rendement: la teneur moyenne du caliche exploité, le prix de revient de l'extraction, et le coût moyen du transport.

Le caliche est transporté à l'usine et déchargé sur le plan incliné de la machine, d'où il tombe directement dans les concasseurs qui le réduisent en morceaux; quelquefois on les fait passer ensuite entre des cylindres afin de rendre leur grosseur uniforme. Au moyen d'appareils appropriés, transporteurs ou élévateurs, le caliche broyé est conduit aux appareils de traitement, où le nitrate sera séparé des autres sels et de la matière insoluble.

La séparation de la matière insoluble, du chlorure et du sulfate de chaux s'effectue au moyen d'un lessivage à l'eau.

D'après les courbes de solubilité (figure 6) on voit que le coefficient de solubilité du nitrate de soude augmente considérablement avec la température, tandis que celui du chlorure reste presque fixe et que celui du sulfate diminue.

Il suffirait donc pour obtenir une dissolution saturée de nitrate de faire la solution à la plus haute température possible entre 110° et 120° centigrades pour que, par refroidissement, le nitrate seul cristallise.

Dans la pratique, les phénomènes ne se passent pas exactement comme la théorie l'indique, et cela pour plusieurs raisons.

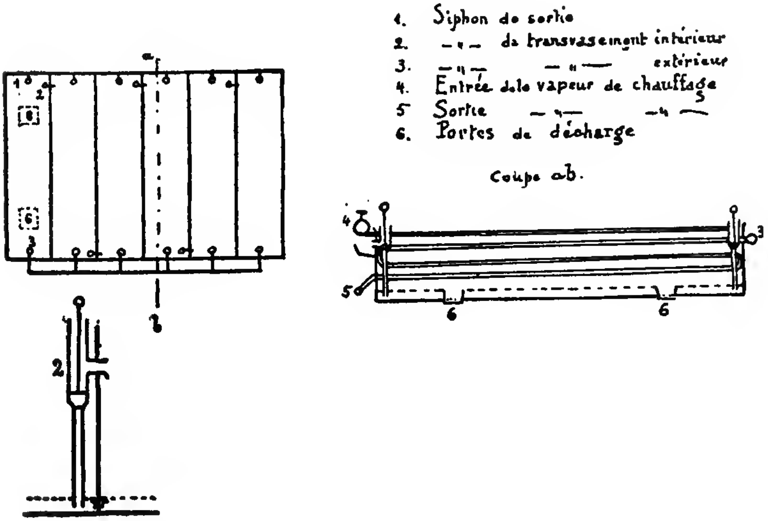
La faible teneur de caliche en nitrate empêche de pouvoir le traiter par la quantité d'eau exactement nécessaire, car il se formerait une boue argileuse qu'il serait impossible de décanter; il est dès lors nécessaire d'employer un excès d'eau.

L'influence perturbatrice des divers sels les uns sur les autres, est cause que les courbes de dissolution ne sont pas les mêmes que lorsqu'il s'agit de matières pures. Si l'on établit les courbes de solubilité expérimentalement, en opérant sur des dissolutions de caliche, on observe de nombreux points d'inflexion, causés sans doute par la formation, au sein du liquide, de sels et d'hydrates complexes.

Enfin l'évaporation continue du liquide pendant tout le traitement, fait qu'il se dépose non seulement du nitrate, mais encore du chlorure et du sulfate au moment de la cristallisation.

Pour remédier en partie à ces inconvénients, on a eu recours au système de lessivage méthodique de Shanks, modifié convenablement par Humberstone. Dans ce système, les liquides suivent une marche à travers une série de bacs—généralement six—en étant, chaque fois, en contact avec des matières différentes à épuiser. Les liquides circulent par gravité, les dissolutions les plus concentrées, sont déplacées par les moins denses; les liquides les plus dilués sont en contact avec la matière la plus épuisée, et le liquide le plus concentré avec celle qui vient d'être chargée; en chauffant convenablement les bacs, on obtient après quatre passages une liqueur concentrée à 110°.

Fig. 7



Les bacs sont de grands récipients rectangulaires de 2 m x 2 m 50 x 10 m, unis entre eux par des siphons de transvasement. Comme on le voit sur la figure 7, chaque récipient a 3 siphons, un de transvasement latéral, un autre de transvasement extérieur, et enfin un siphon de sortie; les bacs ont deux portes de décharge, une sortie inférieure du liquide, un faux fond perforé sur lequel reposent les matières à épuiser, et enfin les serpentins de vapeur pour le chauffage.

Avec un système de 6 récipients ou " cachuchos," on en a quatre en service, un autre en chargement ou prêt au transvasement, et enfin le dernier au lavage ou en déchargement.

La dissolution est controlée au moyen du densimètre et du thermomètre, en suivant des tables dressées par chaque usine; lorsque le liquide possède la concentration nécessaire, on le retire par le siphon de sortie, en ajoutant, comme dans l'opération de transvasement, de l'eau dans le bac de queue, et en cessant immédiatement le chauffage; de cette manière, on lave le caliche épuisé, et le liquide récupère une partie de la chaleur.

Une fois que l'on a extrait le liquide des récipients et fait le transvasement au récipient suivant, le récipient de queue est retiré de la circulation, on le vide par la partie inférieure, et on le lave deux ou trois fois avec de l'eau qui ne contient pas encore de sels en dissolution.

Les eaux de la base, " relaves " sont envoyées dans des réservoirs spéciaux, et sont utilisées pour compenser les pertes d'eau qui se produisent dans le système.

Les liquides concentrés chauds sont, tout d'abord décantés pendant 10 minutes; bien que la circulation des liquides soit très lente, une partie de l'argile est mise en suspension et ne se dépose pas facilement.

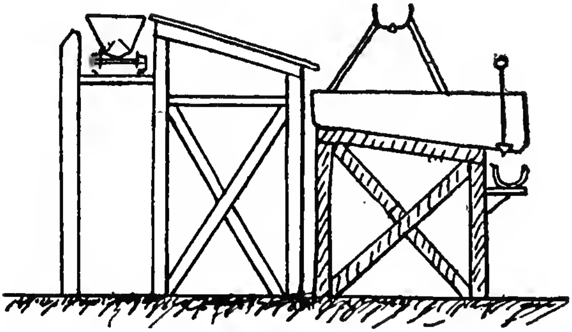
Dans les bacs de décantation appelés " chulladores," les dissolutions sursaturées spécialement en chlorure de sodium s'équilibrent et laissent déposer ces sels.

Des bacs de décantation, le liquide passe aux cristallisoirs, lesquels ont une grande surface et une faible profondeur; la surface est de 20 à 25 mètres carrés et le fond qui est incliné est à une profondeur qui varie entre 2 et 3 mètres.

Les cristallisoirs ou " bateas " sont placés comme on peut le voir figure 8; le plan incliné qui est situé à côté d'eux sert à l'égouttage et au séchage du salpêtre cristallisé. Comme la cristallization exige quelques jours, une partie du liquide s'évapore avec précipitation des sels qu'il dissolvait; on obtient finalement un produit qui contient 95 à 96% de nitrate, 2% d'humidité, 1 à 3% de chlorure, et 0,5 à 1% de sulfate et autres sels.

A la suite des cristallisoirs se trouvent des estacades pour décharger le nitrate et des aires pour le laisser sécher.

Fig. 8.



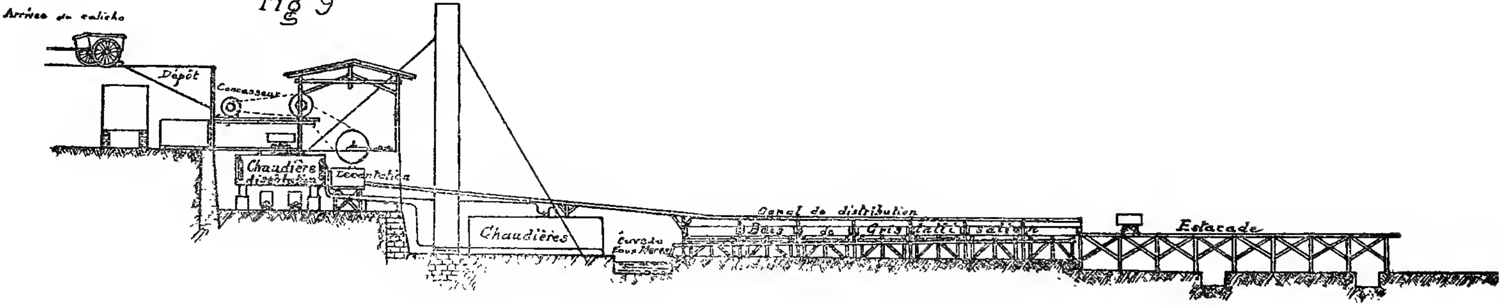
L'ensemble des appareils qui constitue une usine nitratière est représentée par la figure 9. On voit qu'il est besoin de plans disposés en gradin, disposition qu'il n'est pas souvent facile d'obtenir par le niveau du terrain; pour vaincre ces différences de niveau, on a recours aux engins mécaniques: ascenseurs, plans inclinés, etc.

Les résidus de fabrication ou "ripios" sont extraits par la partie inférieure du bac de dissolution, et malgré les lavages spéciaux, ils retiennent toujours une proportion de nitrate qui peut atteindre 8% de leur poids, et qui provient surtout du liquide qui les imprègne.

Il n'est pas possible de laver davantage, car le système actuel de lixiviation ne permet d'employer qu'une certaine quantité d'eau de circulation.

Représentation schématique de la machinerie d'une usine

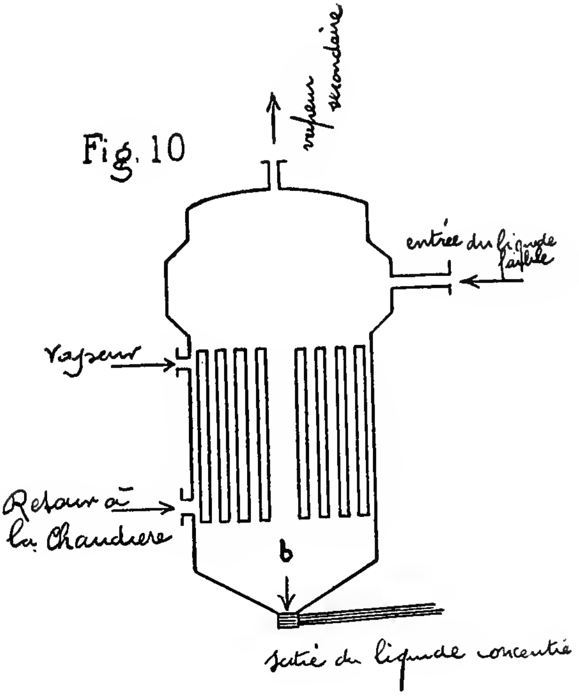
Fig 9



Pour parer à cet inconvénient, et pouvoir laver davantage les résidus du traitement antérieur, certaines usines ont eu recours à des appareils évaporateurs. Les dissolutions très faibles, provenant des lavages plus abondants, sont concentrées dans des appareils " ad hoc "; pendant l'ébullition du liquide, il se dépose une grande quantité de chlorure de sodium et une partie de l'iode est ainsi mise en liberté et entraînée par la vapeur secondaire.

La libération de l'iode, et la grande quantité de sel déposé ont été les deux plus grosses difficultés rencontrées dans l'évaporation des liquides provenant de la dissolution du caliche. Les appareils ont été mis hors d'usage en peu de temps.

Fig. 10



Cependant à la suite de ces premiers essais et en profitant de l'expérience acquise, Messieurs les Ingénieurs Grillo et Perrani ont installé un nouveau système de traitement.

La dissolution du caliche se fait à une température plus basse, environ 80°; les liquides de teneurs faibles en nitrate après décantation sont conduits aux évaporateurs et par ébullition prolongée, concentrés au maximum de dissolution en nitrate; ensuite s'opère la cristallization de la manière courante:

Les évaporateurs à simple effet, sont chauffés directement par les chaudières à basse pression, et la vapeur secondaire débarrassée des vapeurs d'iode, chauffe les bacs de dissolution par simple barbotage.

L'appareil évaporateur utilisé par Grillo et Perrani est représenté par la figure No. 10.

Avec une série de six bacs de dissolution, on peut faire cinq opérations en 24 heures, c'est à dire que l'on retire cinq fois du liquide; chaque bac travaille environ 25 heures de suite. La consommation d'eau varie entre 80 et 150 litres par 100 kilogrammes de nitrate produit; la moyenne de consommation de charbon de toutes les usines est de 25 Kilog. par 100 Kilogs de nitrate.

En général pour produire un minimum de 50,000 quintaux métriques par mois—production courante pour une usine—avec des caliches de 20 à 25%, on a besoin d'un volume de bacs de dissolution égal à 900 mètres cubes; il faut 6,000 métres cubes de bacs de cristallisation. Une usine de cette capacité coùte environ 2,500,000 frs.; il faut, en effet, compter 50 frs. par 100 kilogrammes de production annuelle.

Avec le système employé jusqu'ici, on peut seulement traiter des caliches qui ont au moins 18% de teneur moyenne; le traitement du produit brut est, en effet, réglé pratiquement par le coût du charbon consommé.

Avec des caliches qui ont 50% de nitrate et pas d'insoluble, la consommation de charbon ne dépasse pas 4 Kgs par 100 Kgs de nitrate produit; mais pour la même production, des caliches de 18% consommeraient 25 Kgs de charbon.

Les pertes de chaleur peuvent être classées de la manière suivante:

(a) Chaleur résultant de l'évaporation de l'eau.
(b) Chaleur absorbée et perdue dans les résidus.
(c) Chauffage d'appareils.
(d) Perte due à une élévation de température qui ne cor-

respond pas à une meilleure dissolution plus grande du nitrate.

(e) Pertes par radiation.

En analysant ces pertes, on arrive à la conclusion qu'elles sont d'autant plus grandes que la différence de température entre l'atmosphère et le liquide à la fin de l'opération est elle-même plus grande et que le caliche est plus pauvre.

Le système actual d'élaboration a sa répercussion sur le mode d'extraction du caliche dans le terrain, car il oblige à un triage, ce qui contribue à augmenter la dépense en main d'oevre et exige un amortissement plus rapide du terrain. C'est pour cette cause que le prix de revient de l'azote dans le nitrate de soude est aussi élevé.

Le kilogramme d'azote dans le nitrate de soude mis à bord en sacs sur la côte du Chili, revient au moins à 0,88 frs. et il faut compter sur une moyenne de 1 fr.

Ce prix de revient se répartit ainsi:

Droits d'exportation	41 pour cent
Fournitures (sacs, huile, fourrages, poudre, etc.)	6 pour cent
Transport du produit à bord et commissions	11 pour cent
Administration et frais généraux	3 pour cent
Main d'oeuvre	19 pour cent
Charbon	11 pour cent
Amortissement	9 pour cent

Les quatre premiers nombres sont des variables, indépendants de tous systèmes d'élaboration et d'extraction, très difficiles à réduire, mais, par contre, les trois derniers sont des variables qui dépendant absolument du système actuel de travail et c'est sur leur valeur que l'on doit fixer son attention pour abaisser le prix de revient. On doit chercher des systèmes de traitement qui consomment moins de charbon et exigent moins de main-d'oeuvre.

Le coût du kilogramme d'azote mis en Europe est au minimum de 1 fr 10; la moyenne est d'environ 1 fr 30.

De cet exposé succint de l'état actuel de l'industrie des nitrates au Chili, on peut déduire facilement que le jour est encore loin, où les engrais azotés synthétiques pourront avoir sur elle quelque influence. Bien au contraire, l'industrie chilienne possède le moyen d'obtenir un prix de revient moins élevé, soit en exploitant les terrains encore vierges appartenant à des particuliers ou à l'Etat, soit en améliorant les procédés de traitement ou encore en diminuant les droits d'exportation.

Ces trois éléments ont une grande importance et pris ensemble, ils pourraient déterminer une diminution sensible sur le prix de l'azote nitrique avec lequel mon pays contribue à la consommation du monde.

Le développement de l'industrie nitratière ne peut que croître, car, d'un côté, la consommation du nitrate mondiale, et particulièrement aux Etats Unis, augmente de jour en jour, d'autre part, les nouvelles voies ferrées permettent l'exploitation de terrains très riches qui n'avaient pu être exploités jusqu'à présent vu leur éloignement de toutes les communications.

CONCLUSIONS

I. Les dépôts nitratiers chilien sont susceptibles de fournir toute l'azote nécessaire à l'économie mondiale pour plus d'un siècle.

II. L'industrie qui exploite ces dépôts peut encore se développer et améliorer sa technique.

III. Le prix actuel de revient de l'azote dans le nitrate de soude, peut encore être diminué.

EQUILIBRES DES SYSTEMES : EAU, AZOTITE DE SOUDE ET EAU, AZOTITE DE SOUDE, AZOTATE DE SOUDE

PAR M. MARCEL OSWALD
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La connaissance précise de la solubilité des azotites dans l'eau serait très désirable, à cause de la séparation des mélanges d'azotite et d'azotate par cristallisations, et de l'importance croissante prise par les azotites dans les applications industrielles. Pourtant, aucun travail d'ensemble n'a été publié sur cette question.

Dans le cas de l'azotite de soude, Divers[1] a donné la solubilitè à température ordinaire, soit 83,3 pour 100 d'eau à 15°. J'ai repris cette étude à toutes les températures comprises entre le point d'entexie (- 15°,5) et le point d'ébullition de la solution saturée sous la pression atmosphérique, soit 128° sous 761, 5 mm. Le résultat est le diagramme de la figure 1, où les solubilités sont rapportées à 100 parties d'eau. En portant en abscisses les concentrations de l'azotite dans 100 gr. de solution, on obtient le diagramme de la figure 1 bis; la portion pointillée de la courbe correspond à l'extrapolation de la courbe obtenue jusqu'au point de fusion de l'azotite (219° d'après Divers.[2])

Les équilibres du système ternaire eau, azotite et azotate de soude sont représentés sur la fig. 2. On a porté en abscisses les poids d'azotate et en ordonnées ceux d'azotite dissous dans 100 parties d'eau; on a déterminé les isothermes entre 0° et 103° sous la pression atmosphérique. La courbe A B est le lieu des points où coexistent la solution, l'azotite et l'azotate cristallisés.

De ces courbes résultent les conclusions suivantes: 1° l'azotite de soude ne donne pas d'hydrate stable en solution; 2° l'azotate et l'azotite ne donnent ni composé défini ni cristaux mixtes.

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[1] Journ. of Chem. Soc., LXXV, 1899.

[2] Loc. cit.

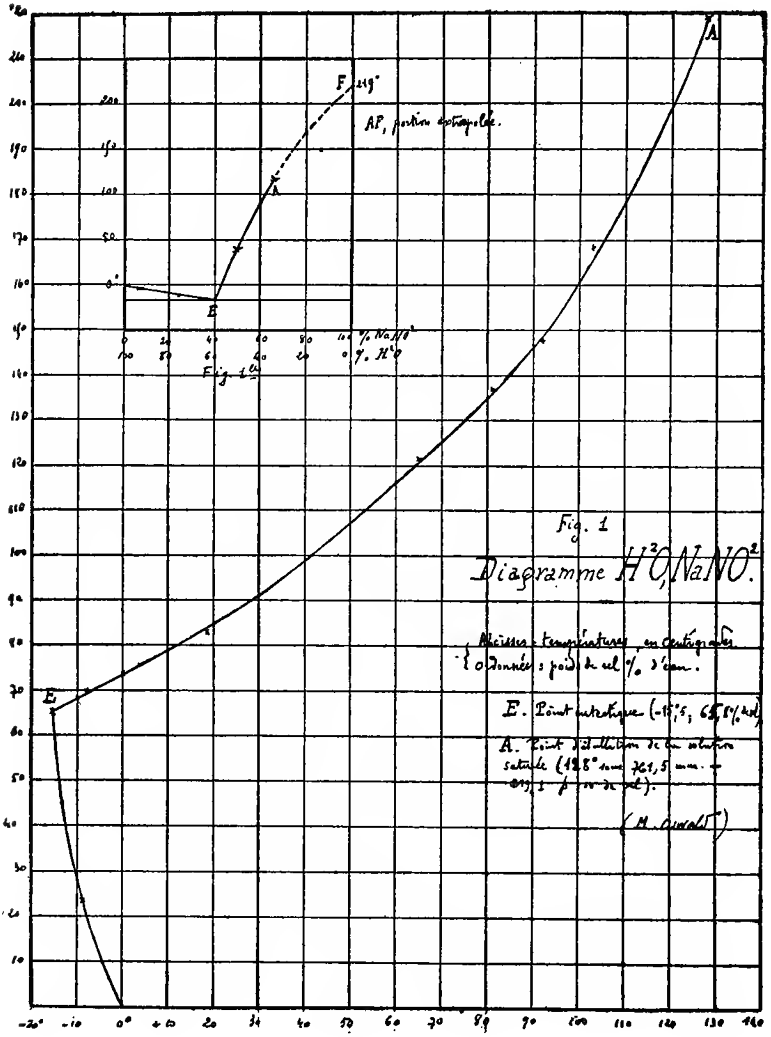
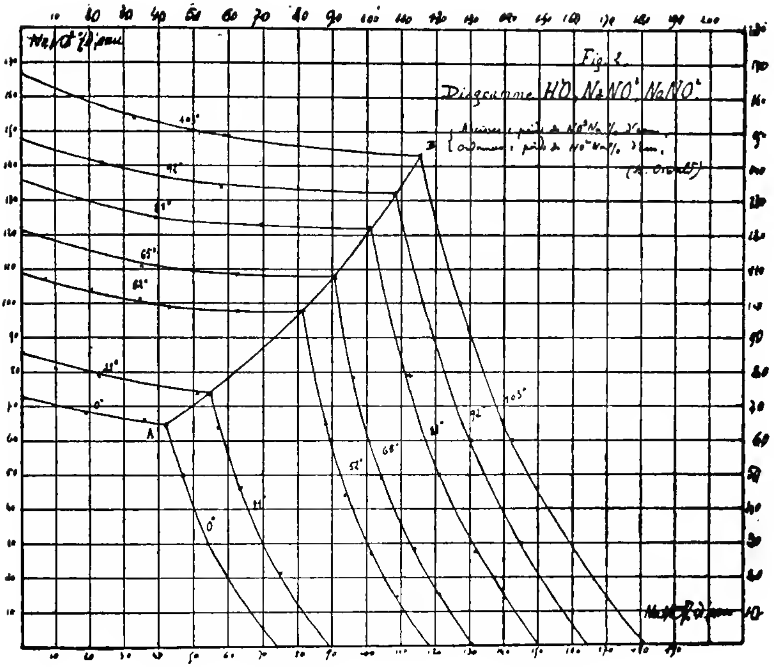


Fig. 1
Diagramme $H^2O, NaNO^2$.
Abcisses : températures en centigrades.
Ordonnées : poids de sel % d'eau.
E. Point eutectique (-15°,5 ; 65,8 % eau)
A. Point d'ébullition de la solution saturée (128° sous 761,5 mm. + 219,1 p. % de sel).
(M. Oswald)
A
E
F 219°
AF, portion extrapolée.
A
E
0°
50
100
150
200
0 20 40 60 80 100 % $NaNO^2$
100 80 60 40 20 0 % H^2O
Fig. 1 bis
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-20° -10 0° +10 20 30 40 50 60 70 80 90 100 110 120 130 140


NaNO² % d'eau
Fig. 2
Diagramme H²O, NaNO³, NaNO²
Abscisses : poids de NO³Na % d'eau
Ordonnées : poids de NO²Na % d'eau
B
A
105°
92°
81°
65°
52°
21°
0°
68°
NaNO³ % d'eau
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

A NEW ALLOY WITH ACID RESISTING PROPERTIES

By S. W. Parr

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While marked advances have been made in the development of alloys with properties which render them resistant to the corroding influence of the atmosphere, not so much study has been given to the production of alloys which would resist the solvent action of strong chemicals. This latter function of resistance to chemical action has been given over almost wholly to the noble metals. However, there are certain specific requirements such as ordinarily call for the use of gold or platinum where the quantity of metal involved and the excessive cost of the same make its use almost prohibitive. These considerations have led to the studies herein described in which the effort has been made to develop an alloy especially resistant to nitric and sulphuric acids.

A preliminary study was first made of certain of the more common alloys with a view to determining their relative solubility in nitric acid. An arbitrary strength of acid was chosen which was obtained by diluting the ordinary strong acid of 1.42 specific gravity in the ratio of 1 of acid to 3 of water making approximately a 25% or 4N solution of HNO_3. The alloys employed together with their order of solubility is shown in Table 1.

Table I. Relative solubility of metals and alloys in 25% HNO_3

		Amount dissolved in 24 hours
1.	Pure iron 99.8 pure	100. %
2.	Commercial Aluminum	51.4%
3.	Monel metal	19.2%
4.	Nichrome Ni 90, Cr 10	7.9%
5.	Copper Aluminum, Cu 90, Al 10	3.5%
	(79) (20) 1	
6.	Nickel chrome aluminum	1.3%
7.	Ferro Silicon	.1%

The tests in Table I were based on the per cent. dissolved in 24 hours at room temperature. They are of value only as they show relative solubilities. Test pieces were used of approximately the same superficial area. The amounts dissolved expressed as percentages are sufficiently accurate for comparison. The range of solubilities varies widely being from 100. to 0.1 per cent.

The last two items on the list suggest the possibility of carrying the series further. Because of its physical characteristics of brittleness, lack of working qualities, etc., the last number, ferro silicon, was not selected as affording an encouraging basis for experimentation. The next to the last number however, the nickel chrome compound with a small amount of aluminum was selected as a suitable type for further study. A series of six mixtures was arranged as in Table II wherein it was sought to determine the effect of the introduction of copper. Some such modifying element seemed necessary for the reason that the value of No. 6 in Table No. 1 was nullified to a large extent by reason of the difficulty experienced in casting that material free from flaws. The melting point of the mixture was extremely high, approximately 1500°, and it was thought that by the introduction of a metal of lower melting point a product would be obtained which would flow more freely and solidify without blow holes. The series arranged, therefore, was a nickel-copper-chrome combination with decreasing amounts of copper and increasing percentages of chrominum as shown in Table II.

TABLE No. II

Series No.	1	2	3	4	5	6
Ni	65	80	80	80	75	70
Cu	30	10	5	5	5	10
Cr	5	10	10	15	20	20
Soluble in 25% HNO_3–24 hours	easily soluble	1.25%	.02%	.05%	.013%	.023%

The interesting fact developed in this series was the degree of resistance that could be attained with considerable quantities of copper present. Nos. 3 and 6 were substantially of the same resistivity but No. 3 was more sluggish in pouring. Very little difference could be detected between Nos. 5 and 6, hence the latter was taken as a basis for further experiments. It was evident from the impossibility of securing perfect cast material from No. 6 that a study must be made of purging agents to clear the bath of oxides and dissolved gases. Aluminum could be used to advantage in this regard while at the same time the resistance to the acids was slightly increased. Tungsten was a slight further aid and manganese up to an amount equaling 1 per cent. did not appreciably augment the solubility factor. Other deoxidizers and denitrifiers in various forms were used such as boron, silicon, titanium and vanadium. The effect of the last one, seemingly, to increase the solubility. The others in fractional percentages, were effective both in improving the resistivity and the texture as well. The average range of values employed was approximately as follows:

TABLE III. Showing Composition of Acid Resistant Alloy

Ni	66.6
Cr	18.
Cu	8.5
W	3.3
Al	2.0
Mn	1.0
Ti	.2
B	.2
Si	.2
	100.0

Not all of the difficulties of casting the material have been eliminated by any means. In proportion as the texture and soundness have been improved upon, the difficulties connected with casting the material have increased. The contraction of the metal at the moment of solidification is very pronounced and shrinkage cracks are very likely to occur. However, these difficulties are chiefly physical and mechanical and in each specific condition they can doubtless be finally overcome. The alloy draws into wire and spins readily and may have numerous interesting applications.

As a method for more precisely measuring the acid resistance of the material, test pieces were prepared having an easily determined superficial area. These pieces were subjected to 4N HNO_3 and in mixtures of nitric and sulphuric acids of similar concentration, for 24 hours at room temperature. The loss in weight was calculated to a unit area of 100 square c. m. per hour. The comparative values are given in Table IV.

TABLE IV. Showing Loss in Milligrams per 100 Square Centimeters per Hour.

No. of Melt	4N HNO_3	4N H_2SO_4	4N HCl	1 Vol. 4N HNO_3 2 Vol. 4N H_2SO_4
23	0.03 m. g.			1.95 m. g.
	0.03	0.79 m. g.	1.95 m. g.	1.98
	0.50			
	0.06			
25	0.19			0.0
	0.08			0.17
40	0.4			0.09
	0.3			0.10
				1.00
54	0.3			0.8
60	0.2			4.8
	0.4			5.2
64	2.0			0.3
	1.85			0.2

The various melts differed slightly in composition, the attempt being made to determine the limits of certain ingredients especially manganese, copper and aluminum. The best results were obtained with compositions conforming most nearly to the values given in Table No. III. The solubility in sulphuric acid was found to be as a rule no greater than in nitric acid, hence,

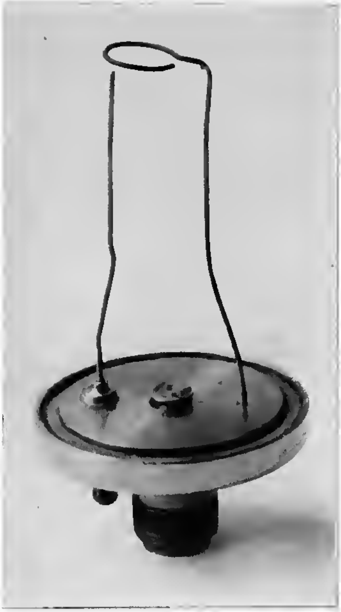

Fig. 1.

the solubility tests were made on mixtures of the two instead of upon the sulphuric acid alone. Very few tests on hydrochloric acid were made. As a rule the solubility of this type of alloy is considerably greater in hydrochloric acid than in nitric or sulphuric acids. Indeed, a study of the various properties of the material up to the present time has been preliminary and largely qualitative. The detailed examination on structure, solubilities, physical and electrolytic properties has been deferred until a practicable or workable alloy could be obtained. This has now been accomplished in a very satisfactory manner and further work as above indicated will be continued. As illustrating the practical value of the alloy a calorimeter bomb was constructed and has already served for heat determinations upon an extended series consisting of sugar, benzoic acid, ethyl-benzene and coals. The pressures employed have ranged from 25 to 50 atmospheres and charges of material up to 1½ grams have been used. The results are all that could be desired. An illustration of the cap or cover to the bomb is given herewith. The interior surface which comes in contact with the corroding gases retains its polish and lustre without any evidence of chemical action. The details of the behavior of the alloy in this apparatus are given in a paper entitled " Some Tests on a New Calorimeter Bomb " by Dr. R. H. Jesse, Jr., presented in Section I of this Congress.

CONTACT SULPHURIC ACID FROM BRIMSTONE

By G. W. Patterson and L. B. Cheney

Indian Head, Ind.

The plant we purpose to describe was erected in 1907 at the U. S. Naval Proving Ground, Indian Head, Md., for the manufacture of acid used in making smokeless powder. It was designed by the New Jersey Zinc Co., which controls the Schroeder patents in this country.

With a rated capacity of six tons, it was operated successfully for three years, burning pyrites from New York and Virginia in O'Brien burners. During the last two years, Louisiana brimstone has been used entirely. The reason for changing raw materials was primarily to increase capacity without enlarging the plant, and it was hoped incidentally to reduce costs, notwithstanding the large increase in price per unit of sulphur. Our expectations have been fully realized in both respects.

The installation will be described under four heads: burner and gas cooling system, gas purifiers, conversion system, and absorbing system. The burner is housed in a detached frame building, 19 ft. x 32 ft., with sulphur store sheds adjacent. A frame building, 52 ft. x 60 ft., contains the conversion and absorbing systems. The gas cooling and purifying systems are in the open at the rear of the two buildings, in part protected by an open shed.

The burner is known as the Tromblee and Paull burner and has been most satisfactory. It consists of a horizontal cylindrical iron shell 8 feet long and 3 feet in diameter with conical ends, revolving on its axis once in two minutes. At one end is a hopper and worm feed with sliding dampers. The other end connects with a rectangular cast iron box of 37 cu. ft. capacity, provided with sliding damper and vertical cast iron uptake pipe. This pipe leads to a brick dust catcher such as is ordinarily used with pyrites burners. The dust catcher merely cools the gas, as no appreciable amount of sulphur is carried beyond the combustion box.

The burner is rated at 5500 lbs. per day, but there has been no difficulty in burning 6000 lbs. per day. Before feeding to the hopper, the sulphur needs no other preparation than breaking up large lumps with a shovel. When forced along by the worm, the sulphur melts just before it drops into the body of the burner, and a sufficient amount of melted sulphur is always present to form a complete liquid coating on the inside of the shell as it revolves. The combustion box and vertical uptake complete perfectly the combustion of any sulphur which is volatilized from the cylinder.

The special advantages of this burner are ease in controlling composition of gas, low cost of upkeep and freedom from losses. Once in about two months it is necessary to clean out the dross which collects in the cylinder. To do this, or to prepare for a shut-down for repairs in any other part of the plant, the sulphur charge is allowed to burn out completely. Any residue in the cylinder is then easily removed by a hoe. Starting the burner after cleaning, or even when it is cold, is a simple operation and no losses occur.

At the exit from the dust catcher the gas has cooled to a temperature of about 230° C. At this point it enters the purifying system, which consists first of 250 lin. ft. of horizontal lead pipe arranged in tiers in a wooden rack. All gas passes through this total length of pipe. This pipe is cooled by a water spray, and here is deposited a small quantity of weak sulphuric acid formed in burning the sulphur. The acid deposited is, however, slight in comparison with the amount collected at the same point when pyrites was burned. The lead pipe connects with a large lead-lined box containing coke and here a further deposit of weak acid is obtained. Up to this point also is formed a slight deposit of carbonaceous matter from the asphaltic material which Louisiana brimstone always carries in small quantities.

From the coke box the gas passes to two wet scrubbers in tandem. Each scrubber outfit consists of a vertical lead cylinder with conical top, about 4 ft. high, a lead pot provided with lead cooling coils for water, and an air lift for circulating constantly a stream of sulphuric acid from the pot to the scrubber. The scrubber is divided horizontally by perforated diaphragms. The acid washes and dries the gas thoroughly and flows out through trapped pipes in a weakened condition to the pot. A pot holds 2500 lbs. of acid and is constantly strengthened to a gravity of 1.75 by the addition of strong acid. The excess acid formed at this point is collected in an egg and can be forced by air pressure to the weak acid supply used in the absorbing system. The air lift was designed by one of us (Patterson) to replace the ordinary bubbler formerly used. Only 5 lbs. air pressure is used, raising 80 lbs. of acid per minute, and the top of the lift is gas-tight, the air being piped to the gas system preventing any loss of SO_2 at this point.

From the scrubbers the gas passes to a second lead-lined coke box exactly like the first one and thence to a pair of dry filters in parallel. Each dry filter consists of three superimposed lead lined iron trays luted together. Each tray contains a mat of dry asbestos fibre supporting a quantity of slag wool. A reserve set of these filters is kept ready for use as they require to be renewed about once in four weeks. The entire charge for two filters is 30 lbs. of asbestos and 400 lbs. of slag wool. The dry filters complete the purification process and the gas is then carried into the main building. Throughout the purification process the gas comes in contact with no other metal than lead, but beyond this point either cast iron or wrought iron is used entirely.

Within the house, the gas first passes through a positive pressure blower, by regulating the speed of which, the composition of the entrance gas is controlled, and the movement of gas through the whole system is completed. Manometers on either side of this blower show a suction of 1.5″ of mercury and a pressure of .75″ of mercury. Just forward of the blower is the sampling pipe where the composition of entrance gas is tested by the usual iodine solution.

The next step in the process is the conversion system which includes a preheater and converter. The preheater is a series of vertical iron U pipes and headers housed in a furnace heated by soft coal to give to the gas an initial temperature of 380° C., this being required for proper catalytic action by the contact mass.

The converter is placed close to the preheater and is a vertical cast iron cylinder 6 ft. in diameter and 8½ ft. high, composed of 5 horizontal sections. Each section contains a wire mesh tray for supporting the contact mass and a baffle to properly spread the gas. The contact mass is anhydrous magnesium sulphate carrying two tenths of one per cent. metallic platinum in finely divided condition. A total quantity of 5900 lbs. of mass which is in coarse granules is spread on the trays to a depth of 14 to 16 inches, leaving a space of about 6 inches between mass sections. The gas enters the bottom of the converter and leaves at the top pyrometer tubes being provided to read the gas temperature before entrance and in each section. From the converter the gas passes through 180 feet of iron pipe to the absorber. This pipe is air cooled in order that the temperature of the gas may be sufficiently low for good absorption.

The absorbing system consists of a tower absorber, an acid cooling pipe, a weak acid mixer and reservoir, a head tank for strong acid, an acid pump, and collecting tank. The tower is a vertical cast iron cylinder 15½ ft. high resting on a cast iron base, the top being covered by a perforated plate from the centre of which rises the exit pipe for waste gases. The tower is lined with acid tile and packed with quartz rock. The gas enters on one side near the bottom. A constant stream of acid is supplied by the pump to the top plate, percolates through the mass of quartz and passes out at the bottom of the tower to the cooling pipe. This is a horizontal water cooled U pipe, one leg of which carries an overflow pipe connecting with the pump and the collector. The acid supplied to the top of the tower is kept at a temperature of 70° C. and has a strength of 99.5% H_2SO_4. The strength of the acid leaving the bottom of the tower is reduced by the constant addition of a small stream of 75% H_2SO_4 just before it enters the cooler.

The reservoir of this weak acid, the mixer and strong acid head tank are mounted on a platform in the center of the building at a sufficient elevation for the acid to flow by gravity. The reservoir is an open lead-lined box holding 1000 gallons. The mixer is a lead pot provided with lead coils for cooling water and a special mixing pipe designed by one of us (Cheney) in which water and strong acid are brought in contact. The mixing pipe consists of two heavy ¾″ lead pipes set at an angle of 30° and held together by a heavy lead sheath burned onto a short length of 1½″ lead pipe. One of the ¾″ pipes carries strong acid from the head tank, and the other ordinary cold water from the mains. The 1½″ pipe serves to carry the hot mixture to the pot without spatter. This type has the advantage of minimum repair and mixes about 5000 lbs. of 75% acid per hour. The head tank has a capacity of 18000 lbs. of strong acid.

The product of the plant passes through a scale tank and is delivered to the nitric acid plant where in winter weather it is mixed with 2 per cent. of nitric acid to prevent freezing. The entire product can be delivered as 99.5% H_2SO_4, but for use in making nitric acid a portion of it is reduced to 94% H_2SO_4.

This being a Government plant the hours of labor for any one shift of men can not exceed eight. The plant is run continuously with three shifts and in addition to the men directly employed in the operation of the plant there is a superintendent who devotes about half of his time to it.

The successful operation of a contact plant, of course, depends largely upon the efficiency of the contact mass. This efficiency is easily influenced by arsenic in the raw materials. Should arseniuretted hydrogen be present in the gas entering the converter, arsenic is deposited on the platinum and is said to " poison " it. The result of " poisoning " is immediately noticeable in the temperature produced by the catalytic action and in the quantity of SO_2 unconverted. Fortunately, this effect may be in part counteracted by raising the temperature of the gases entering the converter, and for this reason hardly any two plants burning pyrites will be found using the same initial temperature. In different plants we have noted temperatures of entrance gas varying from 420° C. to 480° C. The catalytic properties of " poisoned " mass may be improved by sprinkling it with aqua regia and expelling the arsenic by the heat of the converter, or they may be entirely restored by heating the mass in a furnace after sprinkling with aqua regia.

Another factor in conversion is the quantity of SO_2 contained in the gas entering the converter. With pyrites it is customary to use an entrance gas containing not over 5.5 per cent. SO_2 with mass in good condition. When " poisoning " has occurred, this percentage must be reduced to obtain good conversion.

In this plant, using Louisiana brimstone for eighteen months, we have had no indications of " poisoning " and have not opened the converter. The temperature of gas entering the converter is kept constantly at 380° C. and conversions are regularly 95 to 95.5 per cent. This low temperature means a decided saving in coal, and wear and tear on the preheater. During six months the average consumption of coal has been 21.8 lbs. per 100 lbs. of SO_3 made. We believe this to be a figure decidedly less than any Schroeder plant burning pyrites. An entrance gas of 6.5 to 7 per cent. SO_2 is regularly used. During six months under the above conditions, the average make has been a little more than 6 tons of acid a day, and the average yield on sulphur fed to the burner 93.36%. The plant can make a maximum quantity of 8 tons with a yield of 90%. Comparison of cost sheets shows that by changing raw materials from pyrites to brimstone, we have reduced cost of manufacture nearly two dollars per ton of 98% acid; that this reduction is due in part to minimizing losses from shut-downs for repairs, in part to increased yields and in part to saving in coal and cost of upkeep.

DIE PHYSIKALISCHEN UND CHEMISCHEN VORGÄNGE BEIM AUTOGENEN SCHNEIDEN

Von Prof. Dr. A. Stavenhagen
Berlin, Grunewald

Der eigentliche Erfinder des autogenen Schneidens ist der Einbrecher Brown, der 1890 in Hannover mit einer Knallgasflamme die Wand eines Geldschrankes durchlochte. Die ersten autogenen Schneidversuche habe ich 1895 in den Vorlesungen über anorganische Chemie an der Technischen Hochschule zu Berlin ausgeführt.

Da über die chemischen und physikalischen Vorgänge beim autogenen Schneiden recht abweichende Ansichten in Literatur und Technik verbreitet sind, so habe ich diese Vorgänge einem genauen Studium unterzogen und berichte über die Ergebnisse derselben in kurzem wie folgt:

Der Ausdruck "autogenes Schneiden" ist ein wenig glücklich gewählter, weil durch diese Bezeichnung irrige Vorstellungen hervorgerufen werden. Von einem wirklichen "Schneiden" kann bei dem autogenen Schneidverfahren nicht die Rede sein, sondern es handelt sich um Schmelz—und Verbren—nungsprozesse. Es ist allgemein bekannt, dass man einen Körper nur dann verbrennen kann, wenn man ihn zuvor auf seine Entzündungstemperatur erhitzte. Diejenige Substanz, die beim autogenen Schneiden verbrennt, ist Eisen, welches mit einer Knallgasflamme auf die Entzündungstemperatur erhitzt wird. Der Schmelzpunkt reinen Eisens liegt bei ca 1505°; über die Entzündungstemperatur fehlen Angaben. Mit dem Kurlbaum schen Pyrometer habe ich die Entzündungstemperatur des Eisens bei 2200° gefunden. Diese Temperatur ist sicherlich als zu hoch liegend anzusehen, weil die Dissoziation des Wassers bereits bei sehr viel tieferen Temperaturen beginnt und bei 2000° schon ziemlich weit fortgeschritten ist, so dass also höhere Temperaturen als 2000° mit dem Knallgasgebläse nicht zu erreichen sind. Da das Eisen aber im Knallgasgebläse anstandslos verbrennt, so muss die Entzündungstemperatur niedriger als 2000° liegen.

Ein Schmelzen und Verbrennen des Eisens, wie es beim autogenen Schneiden notwendig ist, erreicht man mit der Knallgasflamme und einem Ueberschuss von Sauerstoff unter Druck nur bei denjenigen Eisensorten, deren Schmelzpunkte über ca 1400° liegen; eine Platte aus weissem Gusseisen z. B., das bei 1100° schmilzt, kann mit Hilfe eines Knallgasgebläses nicht durchschnitten werden. Dieser Umstand erklärt sich daraus, dass Gusseisen wohl in der Knallgasflamme schmilzt, wie man sich durch Versuche leicht überzeugen kann, dass es aber zu dem zweiten wichtigen Teile des Schneidprozesses, zum Verbrennen des Eisens in einem Ueberschuss von Sauerstoff, nicht kommt. Die Entzündungstemperatur des Eisens kann nicht erreicht werden, weil zwischen der Entzündungstemperatur des Eisens und dem Schmelzpunkte des Gusseisens ein zu grosses Temperaturintervall, ca 800°, liegt. Solange nicht die ganze Masse des Gusseisens geschmolzen ist, bleibt die Temperatur unverändert, weil die neu zugeführte Wärme verwendet wird, festes Gusseisen in den flüssigen Zustand umzuwandeln. Diese Verwendung der durch die Knallgasflamme zugeführten Wärme dauert so lange, bis alles feste Gusseisen in den flüssigen Zustand übergeführt wird. Eine weitere wichtige Rolle spielt die Wärmeleitung, die sich bei einer niederen Temperatur stärker fühlbar machen muss als bei einer höheren. Die Entzündungstemperatur des Eisens kann also bei einem grösseren Stück. Gusseisen mit der Knallgasflamme nicht erreicht werden. Ein Verbrennen des Eisens durch die Knallgasflamme und Anwendung von Sauerstoff unter Druck tritt nur bei ganz kleinen Gusseisenstücken ein, weil hier die Menge des zu schmelzenden Eisens klein und infolgedessen die Wärmebindung eine geringe ist. In chemischer Beziehung ist auch die Anwesenheit grösserer Kohlenstoffmengen der Verbrennung des Eisens hinderlich, weil die Entzündungstemperatur des Kohlenstoffes unter der des Eisens liegt. Derjenige Stoff wird zuerst verbrannt, dessen Entzündungstemperatur am niedrigsten liegt, und dann der mit der höheren Temperatur. Erst wenn der grösste Teil des im Gusseisen vorhandenen Kohlenstoffes verbrannt ist, wenn also ein Uebergang des

Gusseisens in Stahl bezw. Schmiedeeisen stattge funden hat, findet ein Verbrennen auch von Eisen statt.

Von den chemischen Reaktionen, die für die Wärmebilanz eine Rolle spielen, sind zu erwähnen die Bildung von Wasser, die Bildung von Eisenoxydul, Eisenoxyd, bezw. von Eisenoxyduloxyd und die Bildung von Kohlendioxyd. Die erwähnten chemischen Vorgänge sind exothermische Prozesse, bei denen Wärme frei wird, die für den Fortgang des Schneid-bezw. Schmelzprozesses Verwendung findet, indem sie die Eisenteilchen shcmilzt und auf die Entzündungstemperatur erhitzt. Diese Wärmemenge kommt aber nicht in vollem Ümfange zur Geltung, weil Wärme zur Verdampfung des gebildeten Wassers, zur Dissoziation des Wassers in seine beiden Komponenten und zur Schmelzung der Eisenoxyde verwendet wird.

Die erwähnten chemischen Vorgänge, die den Schneidprozess ungünstig beeinflussen, sind nicht die einzigen, sondern es werden auch beim Verbrennen des Eisens an der Luft nicht unerhebliche Mengen von Stickoxyden gebildet; hier handelt es sich um einen stark endothermischen Prozess. Es sind bereits Patente beschrieben, z. B. das Bendersche Patent D. R. P. No. 192883, bei dem Stickoxyde durch Verbrennen von Kohlenstoff bezw. von Kohlenwasserstoffen in Sauerstoff erzeugt werden. Die Bildung von Stickoxyden tritt nur dann ein, wenn keine reduzierenden Gase zugegen sind, d. h. wenn ein Ueberschuss von Sauerstoff dauernd vorhanden ist. In gleicher Weise erhält man Stickoxyde, wenn Eisen in einem Ueberschuss von Sauerstoff verbrannt wird. Bei dem bekannten Vorgange des Verbrennens einer Uhrfeder in Sauerstoff konnte ich die Bildung von Stickoxyden nicht nachweisen, wohl aber beim Verbrennen von Eisen in einer Knallgasflamme. Es ist ferner bekannt, dass eine in der Luft brennende Knallgasflamme zur Bildung kleiner Mengen von Stickoxyden Veranlassung gibt.

Benutzt man zur Erzeugung der Knallgasflamme nicht reinen Wasserstoff, sondern Acetylen, Leuchtgas, Blaugas etc., so tritt bezüglich der chemischen Reaktionen und der hierdurch gebildeten Stoffe eine wesentliche Aenderung ein. Die Wasserbildung tritt zurück, die Bildung von Kohlendioxyd in den Vordergrund, während die Menge der gebildeten Stickoxyde keinen wesentlichen Schwankungen zu unterliegen scheint.

Interessant gestalten sich die Verbrennungsvorgänge, wenn man statt Wasserstoff Ammoniak oder Kohlenoxyd mit einem Ueberschusse von unter Druck stehendem Sauerstoffe verbrennt. Man ist im stande, auch mit einer Ammoniak-Sauerstoff-flamme dünne Eisenplatten zu durchschneiden. Eine Ammoniak-Sauerstoffflamme erzeugt naturgemäss grössere Mengen von Stickoxyden. Für das Schneiden dickerer Eisenplatten ist Ammoniak nicht verwendbar; der Schneidprozess gelingt aber, wenn dem Ammoniak Wasserstoff zugemischt wird. Die Menge der durch eine Ammoniak-Sauerstoffflamme gebildeten Stickoxyde steigt erheblich bei Gegenwart von brennendem Eisen, wobei die Stickoxyde infolge der raschen Fortführung durch den unter Druck stehenden Sauerstoff nicht leicht der Zersetzung wieder anheimfallen. Verwendet man statt Wasserstoff Kohlenoxyd, so kann Eisen mit einer Sauerstoff - Kohlenoxyd flamme ebenfalls verbrannt werden. In diesem Falle konnten Stickoxyde nicht nachgewiesen werden, ein Umstand, der selbstverständlich erscheint, weil der Stickstoff der Luft sich bei Anwesenheit eines stark reduzierenden Gases, wie Kohlenoxyd, nicht mit Sauerstoff zu vereinigen vermag. Es soll nicht unerwähnt bleiben, dass bei Verwendungeiner Sauerstoff- Kohlenoxydflamme sich kleine Mengen von Cyanverbindungen bilden können.

UEBER DIE ADSORPTION DES EISENPENTACARBONYLS DURCH EISEN

Von A. Stoffel

Amsterdam, Holland

In einer vorigen Abhandlung[1] habe ich einige Mitteilungen gemacht über den Verlauf der von " Mond "[2] und " Berthelot "[3] entdeckten Reaktion zwischen Kohlenoxyd und Eisen, wobei, wie bekannt ist, Eisenpentacarbonyl entsteht, $Fe\,(CO)_5$.

Diese in vielerlei Hinsicht merkwürdige Reaktion, welche auch für die Technik, besonders die Gasindustrie, Bedeutung hat, verlauft bei Zimmertemperatur, wenn auch langsam, doch mit meszbarer Geschwindigkeit; das Eigentümliche aber ist, dasz weder Temperatur-noch Druckerhöhung, wie es scheint, Einflusz ausüben, jedenfalls nicht in dem Masze, wie man es, der Theorie nach, erwarten sollte bei einer Reaktion, welche unter so erheblicher Volumverringerung stattfindet.

Das dieses so ist, geht daraus hervor, dasz man beim Ueberleiten von Kohlenoxyd über Eisen, bei welcher Temperatur man auch arbeitet, immer nur minimale Mengen $Fe\,(CO)_5$ im Dampfe bekommt, und wenn eine bei höheren Temperaturen auftretende Dissociation Ursache davon wäre, so sollte Druckerhöhung jedenfalls die Ausbeute erheblich steigern, und es müszte ein Gebiet von Temperatur und Druck bestehen, innerhalb welches beim Ueberleiten von CO über Eisen leicht gröszere Mengen im Dampfe zu bekommen wären.

Es gelang mir bis jetzt aber nicht ein derartiges Gebiet zu finden, während schon Mond constatirt hat, dasz selbst eine Druckerhöhung bis 10 Atmosphären keine Erhöhung der Ausbeute gab.

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[1] Chemisch Weekbl. 8 pag. 722, 1911.

[2] Journ. chem. soc. 59 pag. 1090, 1891.

[3] Compt. Rend. 112, pag. 1343, 1891.

Auch Dewar and Jones[1], welche die chemischen und physischen Eigenschaften des Eisenpentacarbonyls am eingehendsten studiert haben, konnten nach Ihren eigenen Angaben immer nur geringe Ausbeuten bekommen.

Welche Umstände sind es, welche hier so stark hemmend auftreten?

Ich habe in der oben genannten Publikation eine Antwort auf diese Frage gegeben, und dabei kurz folgendes gefunden: Bringt man Eisen in genügend feiner Verteilung (am besten nach Mond's Verschrift hergestellt) mit CO zusammen, so wird letzteres aufgenommen unter Bildung von $Fe\ (CO)_5$.

Die Geschwindigkeit dieser Aufnahme ist viel gröszer, als man erwarten sollte, und beträgt in den ersten Minuten etwa 10 bis 15 c. c. per Minute und für 100 gram Eisen, entsprechend der Bildung von 15 bis 20 m. Gr. $Fe(CO)_5$. Diese Geschwindigkeit nimmt jedoch schnell ab, ist nach 24 Stunden nur noch + 5 c.c. in die Stunde, und nach einigen Tagen praktisch auf null gesunken. Dann ist etwa $\frac{3}{4}$ L.CO aufgenommen. (berechnet auf 100 gr. Eisen).

Erwärmt man das Eisen auf 100 bis 120°, so destillirt das Eisenpentacarbonyl unter teilweiser Zersetzung aus, und nach Abkühlung auf Zimmertemperatur beginnt die Reaktoin mit derselben Geschwindigkeit wie zuerst. Dieses ist die bekannte Methode zur Darstellung von Mond.

Bestimmt man die Concentration des Carbonyls im Dampfe, nachdem eine gröszere Menge CO aufgenommen ist, so findet man dasz diese nur eine Fraktion des Sättigungsdruckes bei der betreffenden Temperatur ist.

Die Annahme liegt also nahe, dasz es sich heir um eine Adsorption handelt, und dasz also das Eisenpentacarbonyl, welche bei der Reaktion entsteht, von dem Eisen adsorbiert wird, und dasz die dünne Schicht, welche das Eisen bedeckt, den weiteren Verlauf der Reaktion hemmt.

Bei allen Temperaturen bis 60° à 70°, fand ich ungefähr dasselbe; nur bei höheren Temperaturen verhält sich die Sache anders.

Bei 80° hörte die CO Aufnahme schon auf, als nur etwa 80 c. c. aufgenommen waren und bei 100° fand keine Aufnahme mehr statt. Bei diesen Temperaturen musz es die Dissociation sein, welche der Reaktion ein Ende macht.

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[1] Proc. Royal Soc. 76, pag. 558, 1905.

Steigert man bei 80° den Druck, so nimmt zwar die Concentration im Dampfe zu, gleichzeitig aber zeigte es sich, dasz die Hemmung der Reaktion durch die Adsorption auch wiederum auftritt, ebenso gut wie bei niedrigen Temperaturen.

Das Maximum der Concentration des Dampfes bei 80° und ein Atm. Druck war 0.98 vol. %, und bei 100° nur noch 0.21 vol. %. Im Gleichgewichte und wenn eine genügende grosze Oberfläche Eisen vorhanden ist, ist also das Eisenpentacarbonyl bei 80° schon zu 99.02 Vol. % und bei 100° zu 99.79 Vol. % dissociiert. In reinem Zustande dagegen, und ohne eine derartige Katalytisch wirkende Oberfläche findet, wie Dewar und Jones (l. c.) constatirten, gar keine Dissociation statt.

Offenbar handelt es sich hier um eine Art "falsches Gleichgewicht" im Sinne Duhem's.[1] Eine Untersuchung über die von beiden Seiten erreichbaren Gleichgewichte auch bei niedrigen Temperaturen, 60° und 70°, ist jetzt im Gange.

Das Aufhören der Reaktion wird also durch zwei Umstände verursacht, und zwar:

1°. Dissociation, aber nur gegen 80° und höher.
2°. Die Adsorption des $Fe(CO)_5$, durch das Eisen, welche soweit untersucht, bei allen Temperaturen auftrat.

Ich wünsche jetzt über diese Adsorption einige genaueren Angaben mit zu teilen.

Es müszte also bestimmt werden, auf welche Weise die Adsorbierte Menge abhängt von der Concentration des Dampfes, und zwar bei verschiedenen Temperaturen.

Für die Bestimmung der Dampfconcentration arbeitete ich wie folgt:

Ein etwa 160 c. c. fassendes Kölbchen mit rund 100 gr. Eisen (nach Mond's Vorschrift hergestellt) ist verbunden einerseits mit ein em CO haltendes Reservoir welches gestattet die Aufgenommene Menge CO genau zu messen, andrerseits mit einer Flasche von $\pm$ 2 L. Inhalt.

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[1] Duhem Thermedynamique et Chimie 2d Edition, page 462.

Wenn nun eine genügende Menge CO aufgenommen ist, öffnet man den Hahn, welcher Kölbchen und Flasche verbindet, nachdem letztere zuerst mittels der Wasserstrahlluftpumpe evacuiert worden war; der gröszte Teil der Gasmasse flieszt nun aus dem Kölbchen in die Flasche über, wonach sofort der Hahn wieder geschlossen wird.

Nun wird etwas Königswasser in die Flasche eingelassen, dessen Dämpfe schnell das Eisenpentacarbonyl zersetzen, sodasz das Eisen als Oxyd gewogen werden kann.

Eine Wattenpropfen in das Verbindungsrohr verhinderte ein Mechanisches Mitführen von Eisenteilchen aus dem Kölbchen.

An die Flasche war noch ein Manometer angebracht, sodasz das Uebergehen der Gasmasse in die Flasche genau verfolgt werden konnte, und der Hahn nicht länger als nötig war, geöffnet blieb. Auszerdem konnte aus dem Druckunterschied vor und nach das Öffnen des Hahnes die Correction berechnet worden, welche angebracht werden muszte für die im Kölbchen bleibenden Teile der Gasmasse.

Bei geringen Concentrationen und bei gewöhnlicher Temperatur, auch bei gröszerer, haftet dieser Methode keinerlei Fehler an, weildas adsorbierte Carbonyl nur sehr langsam verdampft. Bie höheren Temperaturen aber und gröszeren Concentrationen ist es möglich, dasz bei zu lange geöffnet bleiben des Hahnes, das adsorbierte Carbonyl einfash in die Flasche überdestilliert, und das Resultat also viel u hoch ist.

Die höchsten von mir gefundenen Zahlen stimmen aber gut überein mit den Werten, welche Dewar und Jones (l. c.) für die Concentration des gesättigten Dampfes geben, sodasz auch hier nach obiger Methode richtige Zahlen gefunden werden.

Neben der Concentration des Dampfes ist es noch nötig die von dem Bisen adsorbierte Menge zu kennen. Diese letztere Quantität berechnete ich als die Differenz zwischen totales und gasförmiges Carbonyl. Die totale Menge kann nach zwei Methoden bestimmt werden.

A. Es wird eine gewisse Menge CO aufgenommen, und daraus das Eisenpentacarbonyl berechnet, unter Annahme, dasz alles CO zur Bildung des $Fe(CO)_5$ gebraucht wird.

B. Man läszt eine Menge $Fe(CO)_5$ in einem indifferenten Gase, am besten Wasserstoff, verdampfen und leitet diesen gasstrom durch das Kölbchen, mit Eisen. Die Gewichtszunahme ist dann direkt der totalen Menge $Fe(CO)_5$ gleich.

Die erste Methode ist am leichtesten ausführbar; es blei bt aber dabei unsicher, ob wohl alles CO, welches aufgenommen wird zur Darstellung des Eisenpentacarbonyls gebraucht wird.

Ich habe deshalb zur besseren Kontrolle einige Versuche (in der Tabelle mit + gemerkt) nach der zweiten Methode gemacht, die meisten aber nach der Ersten. Beide gaben nahezu dasselbe Resultat; die nach der zweiten Methode eine etwas niedrige Dampfconcentration bei gleicher adsorbierten Menge.

Ich musz hier aber bemerken, dasz, wo, das eine Mal in CO, das andere in Wasserstoff-Atmosphäre gearbeitet wurde, also die Umstände in beiden Fälle nicht dieselben waren, vollkommene Uebereinstimmung auch nicht erwartet werden kann; groszen Unterschied kann dieses aber nicht geben.

Bei 60° konnte nur die erste Methode gefolgt werden, weil dort schen Concentration auftrat; in CO Atmosphäre konnten noch höhere Concentrationen erreicht werden, wenn auch nicht bis zum Sättigungsdruck, aber in Wasserstoff-Atmosphäre zersetzte das Carbonyl zu schnell, sodasz die zweite Methode hier ganz versagte.

Dasz bei 40° und niedriger dieser Umstand sich nicht zeigte, musg zugeschrieben werden erstens daran, dasz das Gleichgewicht sich zu Gunsten des Carbonyls verschiebt, und zweitens dasz, wenn schen einige Zersetzung auftrat, diese jedenfalls bei diesen Temperaturen zu langsam war, um einigen Einflusz ausüben zu können.

Das Licht wurde bei diesen Arbeiten se gut wie möglich ausgeschlossen, sodasz die Bildung der festen Verbindung $Fe_2(CO)_9$ nicht stattfinden konnte.

Ich fand folgende Zahlen:

19°		41°		60°	
x	c	x	c	x	c
241	0.14	154	0.62	187	2.02
242	0.36	157	0.76	323	5.01
306	0.24	233	0.93	397	8.05
368	0.52	227	1.13	589	1.08
+ 401	0.61	295	1.91	913	15.60
458	1.09	+ 370	2.21	Sättigungsdruck (in% von 1Atm. nach D. und J.)	
589	1.91	422	3.14	19°	3.80
638	2.44	461	3.12	41°	8.20
771	3.08	771	5.84	60°	19.
1209	3.78	1055	7.30		
1384	4.16	1375	8.08		

In dieser Tabelle ist x die adsorbierte Menge, C die Dampfconcentration in Volumprocente.

Wie ersichtlich (Fig. 1) haben die mit diesen Zahlen construirten Kurven genau die Form der Adsorptions-Isothermen,[1] jedenfalls im Anfang bei kleinen Dampfconcentrationen; auch besteht ein stetiger Uebergang der Dampfconcentration in dem Sättigungsdruck.

Bei 60° konnten wie schon gesagt, die Bestimmungen nicht bis zu gröszeren Concentrationen fortgesetzt worden, weil schon Dissociation auftrat.

Wie bekannt ist die Formel für die Adsorptions-isotherme:

$$\frac{x}{m} = \alpha p^{1/n}$$ 1)

werin $\frac{x}{m}$ die pro Fläche-Einheit adsorbierte Menge, p der Dampfdruck, α und n= Constanten sind.

Die Logarithmen der adsorbierten Mengen und Dampfcencentration müssen also linear von Einander abhänger. Bei 19° ist dieses bis 2.44 Vol. % der Fall und bei 41° bis 3.-Vol. %. Im Uebrigen zeigen diese Kurven grosze Aehnlichkeit mit denjenigen welche für Wasserdampf und Baumwolle und Wolle gefunden sind.[2]

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[1] Freundlich Capillarchemie 94,100 und 179.

[2] Orme Masson und E. S. Richards, Proc. Roy. 412 (1907); Travers Proc. Roy. Soc. 79. 204 (1907); Trouton Proc. Roy. Soc. 79 page 383 (1907).

Bei steigender Temperatur nimmt, wie wir sehen, die Dampfconcentration bei gleicher adsorbierten Menge schnell zu, jedoch die Adsorption bleibt bestehen, wenn auch in verminderten Masze, und damit auch die hemmende Wirkung, welche Sie auf die Reaktion ausübt.

Es ist dadurch also genügend erklärt, dasz bei welcher Temperatur man auch arbeitet, immer das Reaktionsprodukt selbst im wachsenden Masze beim Fortschreiten der Reaktion hemmend auftreten kann, und Ursache der geringen Ausbeuten ist, auch bei Höheren Temperaturen.

Erhöhung des Druckes kann unter diesen Umständen keine Besserung geben.

Ueber die Frage in wie weit bei Temperaturen von 100° und höher, wenn durch genügende Druckerhöhung die Dissociation-welche bei einer Atmosphäre und 100° nahezu vollständig ist-zurückgedrängt wird, andere Verhältnisse verliegen, kann jetzt noch nicht gesagt werden, doch ist durch weitere Versuche auf zu klären.

Die Resultate dieser Untersuchung zusammen fassend, haben wir das Folgende:

Es wurde bewiesen, dasz das Eisenpentacarbonyl durch das Eisen adsorbiert wird, und festigestellt, wie die adsorbierte Menge von der Dampfconcentration abhängt bei verschiedenen Temperaturen.

Die Eigentümlichkeit der Reaktion zwischen Eisen und Kohlenoxyd, hauptsächlich die grosze Langsamkeit der Reaktion finde darin eine genügende Erklärung.

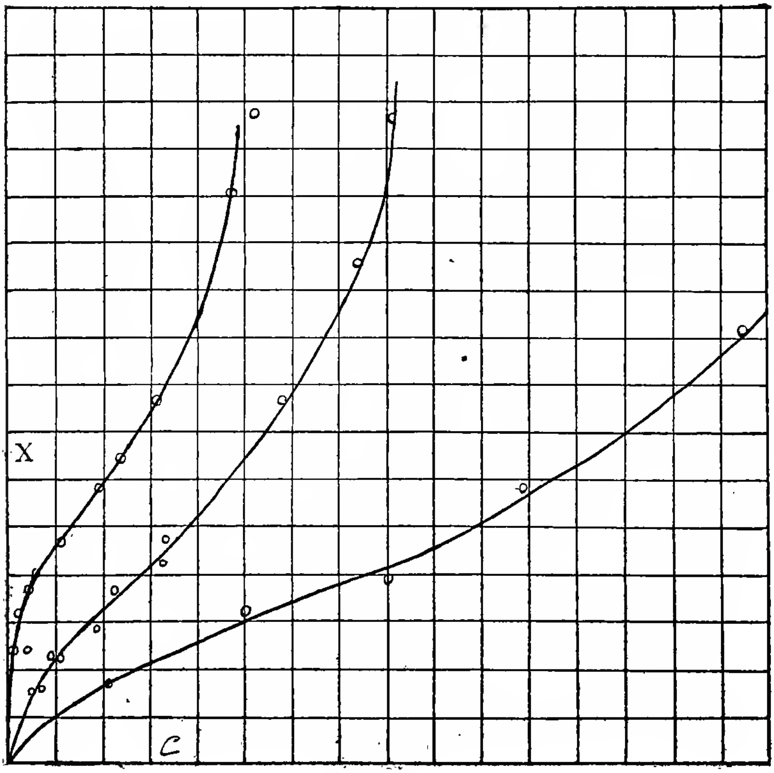

Figure 1.

KURZE INHALT DER VERHANDLUNG UEBER DIE ADSORPTION DES EISENPENTACARBONYLS URCH EISEN

Von A. Stoffel

Es wird zunächst aufmerksam gemacht auf die Eigentümliche Trägheit der Reaktion zwischen Eisen und Kohlenoxyd, welche weder durch Temperatur-noch durch Drucksteigerung shceinbar beeinfluszt wird.

Dann wird der kurze Inhalt wiedergegeben einer Publikation im Chem. Weekbl. 8 pag. 722 (1911), worin als Ursache dieser Trägheit wird angegeben, dasz bei allen Temperaturen eine Adsorption des Eisenpentacarbonyls durch das Eisen stattfindet, während bei höheren Temperaturen, 80° und höher, auch Dissociation auftritt, und zwar zu sehr erheblichen Beträgen; bei 80° befindet sich nur noch 0.98 Vol. %, und bei 100° 0.21 Vol. % $Fe(CO)_5$ im Dampfe.

Dann wird eine Methode beschrieben zur Bestimmung des gasförmigen und des adsorbierten Carbonyls und die nach dieser Methode gefundenen Zahlen, in einer Tabelle vereinigt, mitgeteilt.

Schliesslich werden die mit diesen Zahlen erhaltenen Kurven diskutiert, und dabei festgestellt, dasz Sie genau die Form der Adsorptions-Isothermen aufweisen, sodasz resultirt werden kann, dasz es sich hier wirklich um eine Adsorptionserscheinung handelt, welche diese Reaktion in so hohem Masze beeinfluszt.

ON SILICATES OF SODIUM

By Alb. Vesterberg

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PREPARING AND RECRYSTALLIZATION OF THE METASILICATE OF SODIUM, $Na_2 SiO_3 + 9 H_2O$

In my examinations of resinous acids I found it easier to obtain their salts crystallized and of correct composition, if they were prepared from alcoholic rather than from pure water solutions. Some years ago I accordingly tried to get *silicates* crystallized in the same way. And in fact a salt of the composition $Na_2 SiO_3 + 9 H_2O$ was prepared in the following manner.

One volume of common viscous solution of waterglass, 1 vol. of water, 2 vol. of solution of caustic soda (1,26 sp. gr.) and 2 vol. of alcohol are mixed. The mixture separates in two layers: the upper, about ⅘ of the whole, is a solution of caustic soda, containing but little silicate, in aqueous alcohol; the lower is a viscous layer of a super-saturated solution of silicate of sodium. In both solutions crystallization takes place after a shorter or longer time and finally the bottom layer is nearly solidified to a mass of crystals. This can be recrystallised from a mixture of 10 vol. of water, 1 vol. of caustic soda (1,26) and 2 vol. of alcohol. The crystallization goes on very slowly, but it can be greatly accelerated by adding a little solid salt.

A preparation, which had been twice recrystallized, had the composition marked I, while II is an analysis of another preparation, which had been kept for more than a year in a glass which was not hermetically closed. The substances were very carefully dried by pressing between filter paper. Na_2 O in I was weighed as NaCl, in II it was determined by titration (metylorange).

	I	II	Theoretical for $Na_2SiO_3 + 9\ H_2O$
Na_2O	21,99%	21,58%	21,80%
$Si\ O_2$	21,28%	——	21,20%
$9\ H_2O$	56,70%	56,85%	57,00%

There is then no doubt the salt contains 9 H_2O, and the analysis II shows moreover, that it can be kept in closed vessels for a long time without decomposing.

A silicate of sodium with the same proportion of water has already been described by *J. Fritzsche*[1], who prepared it by " dissolving as much silicious earth in caustic soda, as the solution contains of anhydrous sodiumoxyd." If sufficiently concentrated, the solution solidified after some days to a crystalline mass. After *Fritzsche* nobody seems to have met with a sodiumsilicate with 9 H_2O. And the salts with other proportions of water (5, 6, 7 and 8 H_2O), which are described in the literature, are all of more or less dubious existence, or it has at least not been possible to establish the conditions of their existence. *Abegg* says upon this question in his Handbuch d. anorg. Chemie: " Es sind eine ganze Reihe von Hydraten beschrieben, aber nicht genügend sicher gestellt."

Also *that* crystallized silicate of sodium, which recently *Jordis*[2] has prepared from waterglass with excess of caustic soda, seemed to be no definite hydrate, for *Jordis* found in various preparations the proportion of water varying between 6 and 10 H_2O. Nevertheless these variations, are as I am going to prove, only apparent. Indeed before I had become acquainted with the investigation of *Jordis*, I found that the above mentioned silicate with 9 H_2O could easily be prepared *without* addition of alcohol. One only has to mix one volume of waterglass (I have used a solution with 35,84 g SiO_2 and 11,25 g Na_2O pro 100 c.c.) with one vol. water and two vol. caustic soda (1,26) when, if a little of the salt with 9 H_2O is added, the whole solution will solidify after a few hours. On the other hand *Jordis* has observed, the solution without adding solid salt will remain liquid for a very long time. After rubbing in a mortar the mass of crystals is filtered by suction and recrystallized from a solution containing 2 - 3% caustic soda. The mother-liquor can easily be removed by suction since the salt is not at all viscous.

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[1] At the Versamml.d. Naturforscher zu Bern 1835. See Pogg. Annalen, Bd. 43, 135 (1838).

[2] Zeitschr. anorg. Chemie 56, 296 (1907).

A specimen, which had been recrystallized two times, had the following composition (Na_2O by titration):

	III	IV	Theoretical
Na_2O	21,67%	——	21,80%
9 H_2O	57,02%	57,01%	57,00%

It is thus very probable that *Jordis* had the same salt in his hands, but he did not recognize the real proportion of water in his salts, owing to the unsatisfactory method he applied for drying them before analysis (viz. over chloride of calcium).

According to *Jordis* it would be somewhat precarious to determine alkali by titration in presence of silicious acid, inasmuch as the precipitated silicious acid could absorb alkali. There are, however, no obstacles in such cases, provided that the solution is so diluted, that no precipitation of silicious acid takes place during the titration. No great dilution is needed if the titration is made by 1-10 normal hydrochloric acid.

The salt $Na_2SiO_3 + 9\ H_2O$ is obtained, in the above mentioned manner, partly as crusts of crystals, partly as a beautiful white crystal powder. Easily measurable crystals were obtained by crystallization from strong caustic soda-solution. Mr. *N. Sundius,* who measured them at the Mineralogical Institution of the University of Stockholm proved that they were orthorombic and agreed with the salt of *Fritzsche,* which was measured by *Nordenskiöld.*

The salt melts entirely at about 48° C. although *Fritzsche* states 40°. The salt $Na_2SiO_3 + 8\ H_2O$ of *v. Ammon*[1] was found to melt at about 45°, and *Jordis* had a salt, melting at 36°. The melted salt remains for a long time superfused, if there is no solid salt added.

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[1] Über einige Silikate der Alkalien und Erden. Inaugural-Dissert. Göttingen 1862.

Solubility. The salt dissolves very easily in water with rather great cooling. Thus the coefficient of temperature for solution is positive, and the solubility increases notably with the temperature. On account of the hydrolysis I have examined the solubility not in pure water, but in caustic soda-solution of about ½ normal. For this purpose the salt in excess was shaken many hours with the solution in a rotatory apparatus. The following preliminary results, calculated for 100 c.c. of the solution, were obtained at 17°5 C. (see the following table).

In order to observe the salting-out action of chloride of sodium on the silicate, I examined in the manner just mentioned its solubility both in dilute solution of the chloride (about ½ normal) and by excess of the two salts. For 100 c.c. of the solutions, the results were the following:

	Temp.	Sp. g	Na_2O	SiO_2	$Na_2SiO_3+9H_2O$[1]	NaCl
NaOH, about n/2	17°,5	1,129	6,942 g	5,419 g	25,56 g	——
NaCl, about n/2	17°,5	1,150	7,347 g	7,172 g	33,83 g	2,297g
NaCl in excess	19°	1,258	4,563 g	4,376 g	20,64 g	27,91 g

Thus the salt is more soluble in dilute solutions of chloride of soda, and less soluble in concentrated solutions of the same salt, than in ½ normal solutions of caustic soda. The salting-out action of chloride of soda, however, is not very strong.

OTHER HYDRATES OF THE METASILICATE OF SODIUM

$Na_2SiO_3 + 3\ H_2O$. The crystal water of the silicate $Na_2SiO_3 + 9\ H_2O$ is not lost over caustic soda-solution of 1,26 sp. gr. Moreover the salt can easily and without altering its content of water be recrystallized from soda-solution of this strength, and is easily obtained in measurable crystals (as already noted). A specimen procured in this way had the following composition:

	For $Na_2SiO_3 + 9\ H_2O$
Na_2O — 21,79%	21,80%
$9\ H_2O$ — 57,28%	57,00%

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[1] Calculated from the proportion of SiO_2.

This experiment also proves, that sodium (as earlier found by *Jordis* and others) has no tendency to form *ortho*silicate in the wet way.

The drying of the salt $Na_2SiO_3 + 9\ H_2O$ over caustic potash-lye of 50% goes on slowly. After about two weeks the weight was nearly constant, and the salt had then lost about 37,5% or nearly $\frac{2}{3}$ (i. e. 6 H_2O) of its water. The existence of a salt with 3 H_2O is confirmed by the behaviour of the salt with 9 H_2O being dried over concentrated sulphuric acid. The corresponding curve makes a marked break when the proportion of water remaining has reached 3 H_2O.

$Na_2SiO_3 + 6\ H_2O$. When the salt, which had been dried over concentrated sulphuric acid, and then chiefly contained $Na_2SiO_3 + 3\ H_2O$, was placed over caustic soda of sp. g. 1,26, it rapidly absorbed water, until its content of water had nearly reached 6 H_2O, then more slowly. In this case, however, the break in the curve was much less pronounced than it was for $Na_2SiO_3 + 3\ H_2O$ dried over sulphuric acid, so that the existence of $Na_2SiO_3 + 6\ H_2O$ is less certain than that of $Na_2SiO_3 + 3\ H_2O$. Likewise *Fritzsche* found a crystallized salt with 6 H_2O. But he obtained it only accidentally, so that he could not state its conditions of existence.

Anhydrous Na_2SiO_3. When the salt with 9 H_2O is dried at 100°, 6 H_2O easily go off; then the loss of weight increases but slowly, and the salt is not obtained fully anhydrous, until strongly heated. The anhydrous salt does not melt if heated in a platinum crucible over a common Bunsen flame and only with some difficulty over a Méker or Teclu burner. Hence this substance may be convenient for testing the efficacy of various gas-burners. According to *Kultascheff* the metasilicate of sodium, prepared in the dry way, melts at 1007°.

It is noteworthy, that the melted metasilicate of sodium in the very moment of solidification gives off a quantity of gas, so that the solidified salt, which is clearly crystalline, becomes more or less porous.

THE SULPHURIC ACID INDUSTRY IN THE UNITED STATES

By Utley Wedge

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To arrive at a broad understanding of the sulphuric acid industry in the United States, it is necessary to consider it in its relation to the great industries which require the production of sulphuric acid.

The greatest of these lines of manufacture which require sulphuric acid, are as follows, and opposite each is noted an approximation of the quantity of sulphuric acid consumed in that industry. Figures given are in terms of tons of 50° Be sulphuric acid per annum:

Manufacture of fertilizer	2,400,000 tons
Refining of petroleum products	300,000 tons
Used in iron and steel and coke industry	200,000 tons
Manufacture of nitrocellulose, nitroglycerine, celluloid, etc.	150,000 tons
Manufacture of Aluminum sulphate and the different alums, sulphates of magnesium and similar salts, carbon dioxide and hydrogen, sulphide gas, analin and other organic dies and colors, hydrochloric, nitric, hydrofluoric, chromic, boracic, acetic, picric and other acids, ether, glucose, blue vitriol, zinc sulphates, and in the metallurgy of copper, gold and silver and general chemical practice	200,000 tons
Total	3,250,000 tons

In the manufacture of phosphatic fertilizer, phosphate rock is treated with sulphuric acid to render the phosphoric acid soluble. One ton of rock phosphate requires treatment with about one ton of 50° Be sulphuric acid.

In refining petroleum products, sulphuric acid 66° Be and sometimes fuming acid is used for the removal of tarry matter and to some extent sulphur compounds. For example one thousand barrels of illuminating oil requires for its refining about two tons of oil of vitriol.

In the iron and steel industry, very dilute sulphuric acid, free from arsenic, is used for cleansing steel plates or wire preliminary to galvanizing, making copperas as a by-product; also the steel companies have gone extensively into the production of coke with by-product coke-ovens, one of the products of which is sulphate of ammonia, which requires a little over a long ton of 50° Be sulphuric acid for each net ton of sulphate of ammonia produced.

In the manufacture of nitrocellulose, nitroglycerine, etc., highly concentrated or contact sulphuric acid is used in connection with strong nitric acid to absorb water formed during nitration which would otherwise interfere with the chemical action desired.

In the manufacture of alum, either bauxite or while alumina, are treated with 50° Be sulphuric acid, free from arsenic, to form aluminum sulphate.

In the manufacture of sulphate of ammonia, ammonia gas is absorbed in scrubbing towers by dilute sulphuric acid or solutions of ammonia are treated direct with sulphuric acid.

In the manufacture of blue vitriol, metallic copper is dissolved by hot sulphuric acid, very dilute. Dilute sulphuric acid is also used to some extent in leaching copper ores, concentrates or slimes for the recovery of copper values.

No attempt is made to give a complete category of the uses of sulphuric acid, but enough has been specified so that a reference to the industrial map will show the distribution of lines of manufacture which require sulphuric acid.

Referring to the map it will be seen that phosphate rock deposits are shown in Florida, Tennessee and South Carolina. There are also deposits of phosphate rock in Utah and elsewhere in the Western States which will have great industrial importance as soon as the demand for phosphatic fertilizer in the West has grown to a point to justify the erection of fertilizer plants.

The composition of commercial fertilizer is usually about one-third sulphuric acid, one-third phosphate rock and one-third other components, chiefly filler, with varying amounts of nitrogenous material and potash salts.

The location of fertilizer plants is decided by the following facts:

The phosphate rock has, in any event, either acidulated or not acidulated, to be transported from phosphate deposit to agricultural district where it will be consumed. Filler can be added near the point where the fertilizer will be used. Therefore, the determining factor in the location of phosphatic fertilizer works is the freight on sulphuric acid or crude materials from which it is manufactured.

One ton of pyrites containing 50% sulphur will produce 2.35 tons of 50° Be sulphuric acid, so that it is cheaper to transport iron pyrites than to transport the quantity of 50° Be sulphuric acid which a given amount of iron pyrites would produce.

Sulphuric acid plants in connection with fertilizer plants are therefore generally located adjacent to the agricultural district where the fertilizer will be consumed and not near the deposit of phosphate rock, and combined sulphuric acid and fertilizer plants located near phosphate rock deposits are there merely to supply agricultural requirements in that vicinity. Combined sulphuric acid and fertilizer works are therefore located in parts of the United States where phosphatic fertilizer is required.

Fertilizer is extensively used in connection with the growing of cotton, and by reference to the map, the Southern States denoted as cotton growing states, contain very numerous sulphuric acid plants.

In the Northern and Eastern States, the use of phosphatic fertilizer is not nearly so extensive and a less number of combined sulphuric acid and fertilizer plants supply the demand.

The consumption of fertilizer other than in the Western States, is growing so enormously that a most unusual business situation is developing, and even in Utah, combined sulphuric acid and fertilizer plants are now contemplated.

Much the greater portion of sulphuric acid produced in the United States is made from Iron Pyrites.

In 1911 Spain supplied	815,000 net tons of Pyrites
Portugal	133,000 net tons of Pyrites
United States and Canada about	350,000 net tons of Pyrites
Total	1,298,000 net tons of Pyrites

Of this amount 584,000 net tons was delivered to plants in the South manufacturing sulphuric acid exclusively for the production of fertilizer and 236,000 net tons was delivered to plants in the North manufacturing sulphuric acid exclusively for the production of fertilizer.

These quantities of pyrites would represent a production of sulphuric acid in the fertilizer plants in the Southern States of about 1,300,000 tons of 50° Be sulphuric acid, to which should be added 275,000 tons of 50° Be sulphuric acid produced as a by-product by the copper smelters in Tennessee, practically all of which is consumed in the manufacture of fertilizer in the Southern States.

The 236,000 tons of pyrites delivered to plants in the Northern States manufacturing sulphuric acid exclusively for the production of fertilizer, would represent 529,000 tons of 50° Be sulphuric acid.

In addition to the above fertilizer-acid, considerable quantities of sulphuric acid are manufactured in works doing a general chemical business and shipped to fertilizer works for treatment of phosphate rock, also sulphuric acid separated from sludge acid from petroleum refineries, is shipped in considerable quantities to fertilizer works, bringing the consumption of sulphuric acid in the fertilizer business up to the total figures given above.

In the petroleum industry the consumption of sulphuric acid has increased slowly for some years, for the reason that the oil refiners have learned to economize in sulphuric acid and have decreased the quantity used per barrel in refining to largely offset the large increase in the production of petroleum products. For example, previous to 1888 in many oil refineries sulphuric acid was mixed and stirred with distillate only once, being then at once diluted and separated from the combined tarry matter and again concentrated to 66° Be before using again in the oil refining process. In 1890 the practice came into general use of using sulphuric acid a second time, taking the acid from a previous treatment of distillate and using the partially exhausted acid on a second batch of distillate before separating and concentrating. This materially reduced the consumption of fresh acid. Again, about the year 1896, the use of fullers earth was introduced in oil refining practice. Tarry matter was removed from distillate by agitation with fullers earth and a decreased amount of work remained to be done by sulphuric acid treatment. These two improvements made a material reduction in the use of sulphuric acid in oil refining. Subsequent improvements in method and practice in recovering sulphuric acid from sludge or spent acid have further reduced the net consumption of fresh sulphuric acid by the petroleum industry.

The location of acid plants supplying oil refineries is quite uniformly adjacent to the oil refineries on account of the transportation problem.

Transportation of crude oil by pipe line is so much cheaper than the transportation of refined products by rail, that oil refineries under conditions in the United States are located with reference to transportation and distribution of the refined product and seldom adjacent to oil producing fields, except only to supply the demand for the finished product in the radius of economic shipment from the oil fields. The great oil refineries are therefore chiefly located where there is both rail and water transportation. The map shows oil fields in Pennsylvania, Ohio, Indiana, West Virginia, Indian Territory, Texas, California and some other states. The large oil refineries, however, are located along the Atlantic seaboard on the water front near New York harbor, Philadelphia and Baltimore; along the Great Lakes at Buffalo, Cleveland and near Chicago; on the Pacific Coast on San Francisco Bay. Minor oil refineries are located near the oil fields. In every case sulphuric acid plants are located near the oil refineries. The group near New York are supplied from a large chamber-process sulphuric acid plant on New York harbor, operated by the petroleum refining interest, with an output of about 60,000 tons of oil of vitriol per annum. Oil refineries at Philadelphia and Baltimore are supplied with oil of vitriol from a sulphuric acid plant at Philadelphia delivering about 40,000 tons of oil of vitriol per annum. The California crude oil requires treatment in part with an acid stronger than oil of vitriol, which is supplied from an oxide-of-iron-contact plant at the oil refinery, on San Francisco Bay.

One small oil refinery adjacent to the Texas oil fields burns brimstone from the Louisiana sulphur deposit.

In many cases, the oil refineries or chemical companies supplying them with sulphuric acid are equipped with appliances for separating sulphuric acid from the tarry matter taken up in the treatment of petroleum distillates and the separated acid of 35° Be to 50° Be is then again concentrated to 66° Be for further use. This repeated restoring of the spent acid greatly diminishes the amount of fresh sulphuric acid required by the petroleum industry and brings their net requirements down to the figure given above.

Mention should also be made of a practice by the petroleum refiners to a very limited extent of manufacturing sulphuric acid from sulphuretted hydrogen and sulphur dioxide fumes given off during the distillation of petroleums high in sulphur contents. In general, it may be said that the fresh sulphuric acid consumption by the petroleum refining companies represents chiefly the actual decomposition of a percentage of the sulphuric acid used by reduction to SO_2 by the carbon in the oil treated, plus deliveries of separated sulphuric acid 50° Be gravity to fertilizer plants. In addition to the mechanical loss in use, there is actual decomposition to SO_2 during treatment, especially of heavy oils, and also the decomposition is considerable in the process of separating and reconcentrating the sulphuric acid.

Counting the repeated use of sulphuric acid by the petroleum industry, their actual use of oil of vitriol would be about 334,000 tons per annum, representing 500,000 tons of 50° Be equivalent.

The iron and steel industry uses such considerable amounts of sulphuric acid that a tendency is developing for steel companies to erect and operate separate sulphuric acid plants. The manufacture of sulphate of ammonia from by-product coke-ovens has been taken up by the steel companies.

A coke plant consuming 2000 tons of coal per day would produce from 14 to 30 tons of sulphate of ammonia daily, according to the nitrogen content of the coal used. Therefore, each 2000 tons of coal, high in nitrogen, converted into coke daily, would call for a sulphuric acid production of 10,000 tons of 50° Be sulphuric acid per annum.

The location of sulphuric acid plants to supply this demand has so far been adjacent to the steel plants in Pennsylvania, Indiana, Michigan and Alabama.

By-product coke-ovens are now constructing or under consideration which will require 100,000 to 150,000 tons of 50° Be sulphuric acid per annum, in addition to the figure shown above. This development has so far been chiefly in connection with the iron and steel industry.

One of the sulphuric acid plants operated by one of the steel companies burns brimstone from Louisiana; the others burn pyrites. All so far constructed, have been chamber-plants, although one by-product plant now constructing has contracted for its supply of sulphuric acid from a concern producing contact acid.

In the manufacture of nitrocellulose, nitroglycerine and similar products, the chamber-process has been practically eliminated by the contact process. Contact processes have been installed wherever these explosives are manufactured. Several iron-oxide contact plants have been erected for this purpose as well as other contact systems.

In the general chemical industry, the various platinum and iron contact systems have made considerable progress, more especially where the demand is for sulphuric acid approaching the composition of the monohydrate.

Out of a total production of sulphuric acid in the United States of 3,250,000 net tons per annum, approximately ten per cent. (10%) is contact acid made either by the iron-oxide contact or by the platinum contact systems.

Of the Spanish pyrites imported during 1911, namely 815,000 tons, 37% was copper bearing pyrites, of which about 200,000 tons were chloridized and leached for the recovery of copper values, after burning off the sulphur for the manufacture of sulphuric acid.

Of the 646,000 tons of iron pyrites imported during 1911 containing no copper values, about 230,000 tons was washed fines from which copper had been leached in Spain or Portugal before shipment to this country.

The practice of nodulizing cinder from pyrites burners has become general in all localities where there is a market for the nodulized cinder as iron ore. The iron industry of Pennsylvania furnishes a good market. In Alabama the iron manufacturers have not as yet offered prices for low phosphorus nodulized cinder such as to make profitable the installation of nodulizing kilns and there is in the South the accumulated cinder from years of sulphuric acid manufacture, waiting for prices which will make its utilization profitable.

An analysis of the source of sulphuric acid manufactured in the United States during 1911 would show as follows, figures given being expressed in terms of 50° Be sulphuric acid:

Manufactured from pyrites	2,665,000 tons
Manufactured from blast furnaces, smelting copper sulphide ores	275,000 tons
Manufactured from zinc sulphide ores	285,000 tons
Manufactured from brimstone	25,000 tons
Total	3,250,000 tons

COMBINATION OF THE CONTACT PROCESS WITH THE ORDINARY LEAD CHAMBER OR TOWER SYSTEMS; AN IMPROVEMENT IN THE MANUFACTURE OF SULPHURIC ACID

By William Wilke

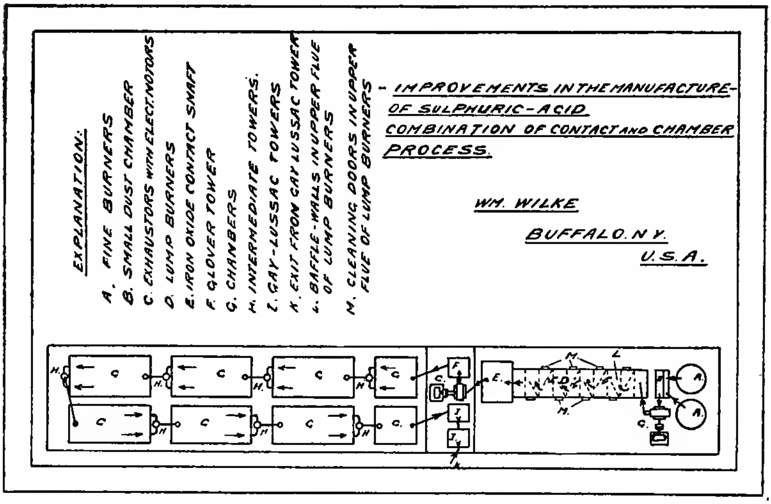
Buffalo, N. Y.

Since the introduction of the Contact System as a practical method for making Sulphuric Acid, it has been usually regarded as simply a competitor of the older chamber or tower systems. It may be of interest to bring before you a system in which the Contact function is combined with the chamber system, giving a successful working method that shows economies and advantages not generally appreciated but very worthy of attention.

Some time ago I was called upon to construct a Chemical Works which should be thoroughly equipped for the manufacture of Mineral-Acids—the main problem involved being the construction of a plant wherein Sulphuric Acid of the various commercial grades and concentrations could be manufactured in the most economical way. My clients had already an installation of the Contact Process licensed under U. S. Patents of the Verein Chemischer Fabriken in Mannheim, for the production of Strong Acid, and the question arose whether we could economically and profitably reduce this highly concentrated acid to lower strengths.

In calculating the cost we have to take into consideration the License-Fee and other fixed charges, and it was found in the end that it was impossible to do this. There was however a market for Chamber Acid; consequently it was thought possible to combine the Contact Process with the Chamber Process and attain the end in view.

As a result of the study of conditions, a plant was designed as shown in the illustration. In order to be independent of the constant variations in the Pyrites Market and the possible scarcity of Pyrite Fines, the plant was so designed that Lump Ore as well as Fines could be roasted, the burning capacity finally adopted being 24,000 lbs. Fines and 36,000 Lump Ore. Thirty-six lump burners were installed, each able to handle from 900 to 1200 lbs. ore daily, and four standard Herreshoff fines burners.


EXPLANATION:
A. FINE BURNERS
B. SMALL DUST CHAMBER
C. EXHAUSTORS WITH ELECTR. MOTORS
D. LUMP BURNERS
E. IRON OXIDE CONTACT SHAFT
F. GLOVER TOWER
G. CHAMBERS
H. INTERMEDIATE TOWERS.
I. GAY-LUSSAC TOWERS
K. EXIT FROM GAY LUSSAC TOWER
L. BAFFLE-WALLS IN UPPER FLUE OF LUMP BURNERS
M. CLEANING DOORS IN UPPER FLUE OF LUMP BURNERS
- IMPROVEMENTS IN THE MANUFACTURE OF SULPHURIC-ACID
COMBINATION OF CONTACT AND CHAMBER PROCESS.
WM. WILKE
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The gases from the fines burners were conducted into a flue situated above the flue of the lump burners and provided with a number of baffle walls to catch some of the dust. The gases of the lump burners and fines burners were united and conducted into the pateted Iron-Oxide-Contact-Shaft, similar to the Contact Process chamber of the Verein Chemischer Fabriken. In order to regulate the draft on the fines burners, a separate Exhaust Fan was installed to draw the gases from the fines burners and deliver them into the flue over the lump burners. A second Exhaust Fan was installed between the Iron-Oxide-Contact-Shaft and the Glover Tower, which took the Sulphurous Gases after they had undergone conversion, to the extent of 30%, into SO_3 by the Iron-Oxide-Contact-Shaft and forced them through the Glover Tower into the Chamber System.

The combination of the two very distinct processes into one system gave most excellent results. It was found that:

1. The capacity of the chamber plant was increased at least 30%.
2. That the Conversion of SO_2 to SO_3 in the Iron-Oxide-Contact-Shaft averaged about 30%.
3. That at the same time the acid produced in the Glover tower was water-white.
4. That 95% of the Arsenic carried by the gases leaving the roasters and flues was eliminated by means of the Iron Oxide,

and finally it was proved

5. That the total production of the Chamber System could easily be concentrated to 60° Baume or higher in the Glover tower.

Such satisfactory results are all attributable to the introduction of the Iron-Oxide-Contact-Shaft between the burners and the Glover tower; in other words, to the suitable combination of the Contact and the Lead Chamber Processes.

The Iron-Oxide-Contact-Shaft retards the dust and is the best known means of keeping dust from getting into the Chamber System; it is an accumulator of heat and acts as an equalizer on any system, such as that described, enabling the operator of the plant to carry out the process more uniformly; it saves 30% of the Nitre consumed in the ordinary plant, on account of the conversion by the Catalytic Action.

Since constructing the above described plant, the Iron-Oxide-Contact-Shaft has been introduced in other existing Chamber plants with equally good results.

(*Abstract*)

THE EFFECT OF "LIME-SULPHUR SPRAY MANUFACTURE" ON THE EYE SIGHT

By James R. Withrow

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Attention is called to some manufacturing experiences with Lime-Sulphur Spray manufacture. Articles discussing lime-sulphur preparation from lime, sulphur and water, do not mention any discomforts arising. This was probably because of the small scale on which most of the work was done. The author found no trouble on a small scale. On the factory scale, however, the eyesight was temporarily and sometimes painfully affected, when thorough ventilation during boiling, was not maintained. A polysulphide of hydrogen is suggested as the cause of the effect on the eyes. The remedy for the condition during manufacture was found to be hood-covered boiling tanks, and ample ventilation at all times.

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